

NURTURE COURSE
ATOMIC STRUCTURE

ATOMIC STRUCTURE

1. INTRODUCTION :

The existence of atoms has been proposed since the time of early Indian and Greek philosophers (400 B.C.) who were of the view that atoms are the fundamental building blocks of matter. According to them, the continued subdivisions of matter would ultimately yield atoms which would not be further divisible. The word 'atom' has been derived from the Greek word 'a-tomio' which means 'uncuttable' or 'non-divisible'. These earlier ideas were mere speculations and there was no way to test them experimentally. These ideas remained dormant for a very long time and were revived again by scientists in the nineteenth century. The atomic theory of matter was first proposed on a firm scientific basis by **John Dalton**, a British school teacher in 1808. His theory, called **Dalton's atomic theory**, regarded the atom as the ultimate particle of matter.

2. DALTON ATOMIC THEORY :

- (i) Atom is the smallest particle of any substance which cannot be divided further.
- (ii) Atoms can never be created nor be destroyed. Only the rearrangement of atoms occurs in chemical reactions.
- (iii) All the atoms are hard and dense.
- (iv) All the atoms of an element are identical but the atoms of different elements will be different.
- (v) A compound is formed by the combinations of atoms of different elements in a fixed ratio by mass.

We start with the experimental observations made by scientists towards the end of nineteenth and beginning of twentieth century. These established that atoms can be further divided into subatomic particles, i.e., electrons, protons and neutrons. a concept very different from that of Dalton. The major problems before the scientists at that time were:

- to account for the stability of atom after the discovery of sub-atomic particles,
- to compare the behaviour of one element from other in terms of both physical and chemical properties,
- to explain the formation of different kinds of molecules by the combination of different atoms and,
- to understand the origin and nature of the characteristics of electromagnetic radiation absorbed or emitted by atoms.

3. SUB-ATOMIC PARTICLES

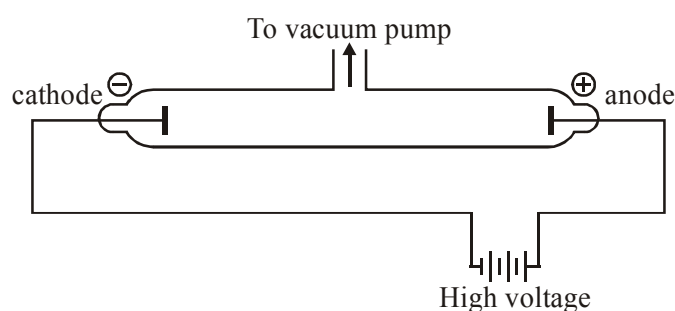
Dalton's atomic theory was able to explain the law of conservation of mass, law of constant composition and law of multiple proportion very successfully. However, it failed to explain the results of many experiments, for example, it was known that substances like glass or ebonite when rubbed with silk or fur generate electricity. Many different kinds of sub-atomic particles were discovered in the twentieth century.

3.1 Discovery of Electron :

In 1830, Michael Faraday showed that if electricity is passed through a solution of an electrolyte, chemical reactions occurred at the electrodes, which resulted in the liberation and deposition of matter at the electrodes. These results suggested the particulate nature of electricity.

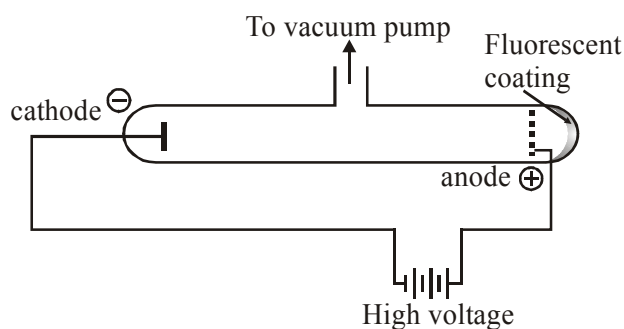
An insight into the structure of atom was obtained from the experiments on electrical discharge through gases. Before we discuss these results we need to keep in mind a basic rule regarding the behaviour of charged particles: "Like charges repel each other and unlike charges attract each other".

In mid 1850s many scientists mainly Faraday began to study electrical discharge in partially evacuated tubes, known as **cathode ray discharge tubes**.



A cathode ray discharge tube

A cathode ray tube is made of glass containing two thin pieces of metal, called electrodes, sealed in it. The electrical discharge through the gases could be observed only at very low pressures and at very high voltages. The pressure of different gases could be adjusted by evacuation. When sufficiently high voltage is applied across the electrodes, current starts flowing through a stream of particles moving in the tube from the negative electrode (cathode) to the positive electrode (anode). These were called **cathode rays or cathode ray particles**. The flow of current from cathode to anode was further checked by making a hole in the anode and coating the tube behind anode with phosphorescent material zinc sulphide. When these rays, after passing through anode, strike the zinc sulphide coating, a bright spot on the coating is developed (same thing happens in a television set)



A cathode ray discharge tube with perforated anode

The results of these experiments are summarised below.

- (i) The cathode rays start from cathode and move towards the anode.
- (ii) These rays themselves are not visible but their behaviour can be observed with the help of certain kind of materials (fluorescent or phosphorescent) which glow when hit by them. Television picture tubes are cathode ray tubes and television pictures result due to fluorescence on the television screen coated with certain fluorescent or phosphorescent materials.

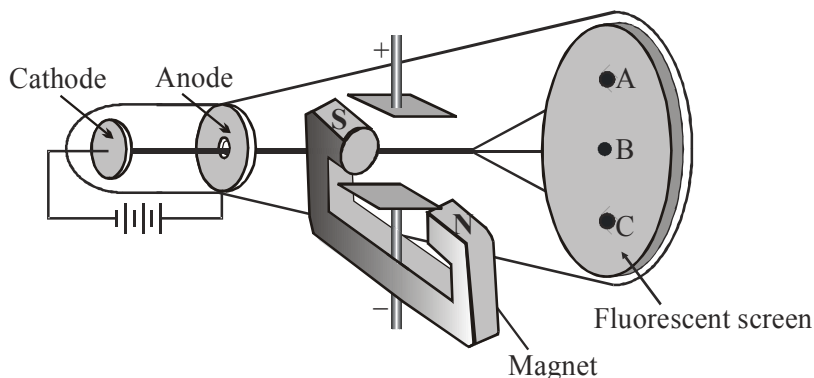
- (iii) In the absence of electrical or magnetic field, these rays travel in straight lines.
- (iv) In the presence of electrical or magnetic field, the behaviour of cathode rays are similar to that expected from negatively charged particles, suggesting that the cathode rays consist of negatively charged particles, called **electrons**.
- (v) The characteristics of cathode rays (electrons) do not depend upon the material of electrodes and the nature of the gas present in the cathode ray tube.

Thus, we can conclude that electrons are basic constituent of all the atoms.

3.1.1 Charge to Mass Ratio of Electron :

In 1897, British physicist J.J. Thomson measured the ratio of electrical charge (e) to the mass of electron (m_e) by using cathode ray tube and applying electrical and magnetic field perpendicular to each other as well as to the path of electrons. Thomson argued that the amount of deviation of the particles from their path in the presence of electrical or magnetic field depends upon :

- (i) the magnitude of the negative charge on the particle, greater the magnitude of the charge on the particle, greater is the interaction with the electric or magnetic field and thus greater is the deflection.
- (ii) the mass of the particle lighter the particle, greater the deflection.
- (iii) the strength of the electrical or magnetic field. the deflection of electrons from its original path increases with the increase in the voltage across the electrodes, or the strength of the magnetic field.



The apparatus to determine the charge to the mass ratio of electron

When only electric field is applied, the electrons deviate from their path and hit the cathode ray tube at point A. Similarly when only magnetic field is applied, electron strikes the cathode ray tube at point C. By carefully balancing the electrical and magnetic field strength, it is possible to bring back the electron to the path followed as in the absence of electric or magnetic field and they hit the screen at point B. By carrying out accurate measurements on the amount of deflections observed by the electrons on the electric field strength or magnetic field strength, Thomson was able to determine the value of e/m_e as:

$$\frac{e}{m_e} = 1.758820 \times 10^{11} \text{ C kg}^{-1}$$

where m_e is the mass of the electron in kg and e is the magnitude of the charge on the electron in coulomb (C). Since electrons are negatively charged, the charge on electron is $-e$.

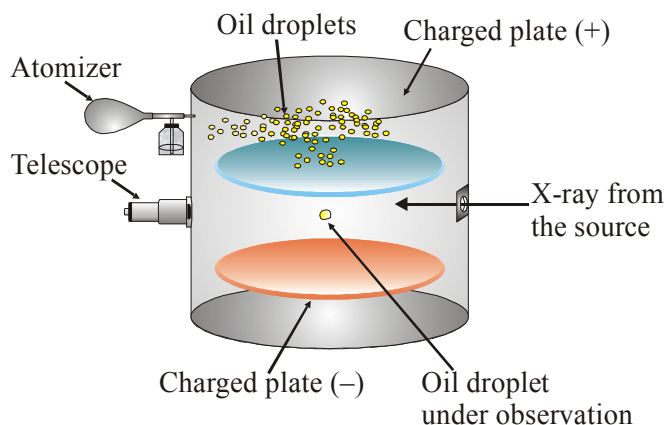
3.1.2 Charge on the Electron :

R.A. Millikan (1868-1953) devised a method known as oil drop experiment (1906-14), to determine the charge on the electrons. He found that the charge on the electron to be -1.6×10^{-19} C. The present accepted value of electrical charge is -1.6022×10^{-19} C. The mass of the electron (m_e) was determined by combining these results with Thomson's value of e/m ratio.

$$m_e = \frac{e}{e/m_e} = \frac{1.6022 \times 10^{-19} \text{ C}}{1.758820 \times 10^{11} \text{ C kg}^{-1}} = 9.1094 \times 10^{-31} \text{ kg}$$

Millikan's Oil Drop Method

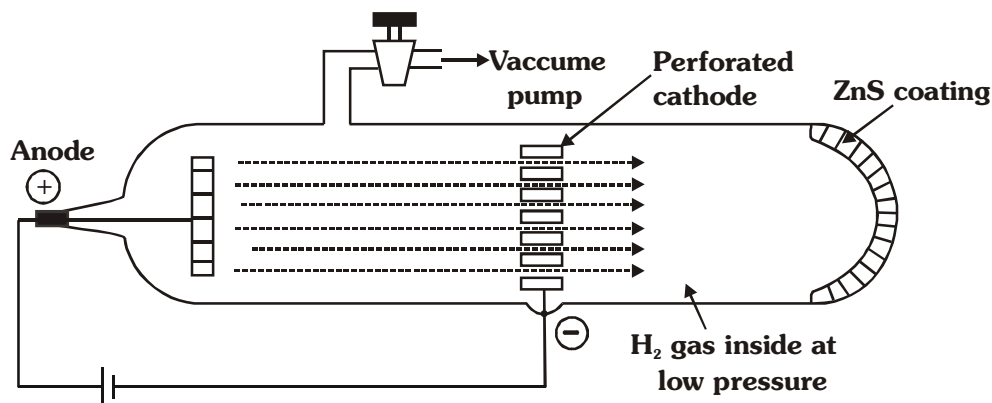
In this method, oil droplets in the form of mist, produced by the atomiser, were allowed to enter through a tiny hole in the upper plate of electrical condenser. The downward motion of these droplets was viewed through the telescope, equipped with a micrometer eye piece. By measuring the rate of fall of these droplets, Millikan was able to measure the mass of oil droplets. The air inside the chamber was ionized by passing a beam of X-rays through it. The electrical charge on these oil droplets was acquired by collisions with gaseous ions. The fall of these charged oil droplets can be retarded, accelerated or made stationary depending upon the charge on the droplets and the polarity and strength of the voltage applied to the plate. By carefully measuring the effects of electrical field strength on the motion of oil droplets, Millikan concluded that the magnitude of electrical charge, q , on the droplets is always an integral multiple of the electrical charge, e , that is, $q = n e$, where $n = 1, 2, 3 \dots$. The highest common factor (HCF) of charges on oil droplet was taken as charge on electron.



The Millikan oil drop apparatus for measuring charge 'e'. In chamber, the forces acting on oil drop are: gravitational, electrostatic due to electrical field and a viscous drag force when the oil drop is moving.

3.2 CANAL RAYS (OR ANODE RAYS) – DISCOVERY OF PROTON :

Atoms are electrically neutral. Hence after the discovery of the negatively charged constituent (electron) of an atom, attempts were made to discover the positively charged counterpart of electrons. By using a discharge tube containing a perforated cathode, **Goldstein (1886)** found that some rays passed through these holes in a direction opposite to that of the cathode rays.



Positive Rays or Canal Rays

Electrical discharge carried out in the modified cathode ray tube led to the discovery of particles carrying positive charge, also known as **canal rays**. The characteristics of these positively charged particles are listed below.

- unlike cathode rays, the positively charged particles depend upon the nature of gas present in the cathode ray tube. These are simply the positively charged gaseous ions.
- The charge to mass ratio of the particles is found to depend on the gas from which these originate.
- Some of the positively charged particles carry a multiple of the fundamental unit of electrical charge.
- The behaviour of these particles in the magnetic or electrical field is opposite to that observed for electron or cathode rays.

The smallest and lightest positive ion was obtained from hydrogen and was called proton. This positively charged particle was characterised in 1919.

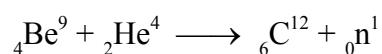
The lightest positively charged particle is called a proton (P or P⁺). Positive rays are atomic or molecular cations from which some electrons have been removed. The removed electrons constitute the cathode rays and the positive cations form the positive or canal rays.

3.3 DISCOVERY OF NEUTRON :

After the discovery of electron and proton **Rutherford (1920)** predicted the existence of a neutral fundamental particle. In **1932, Chadwick** bombarded the element Beryllium with α -particles and noticed the emission of a radiation having the following characteristics.

- The radiation was highly penetrating.
- The radiation was unaffected by magnetic and electric fields which shows that it is electrically neutral.
- It was found to have approximately the same mass as the protons.

The name 'neutron' was given to this sub-atomic particle. It is denoted by n or ${}_0n^1$. Bombardment of beryllium by α -particles results in the formation of carbon and neutrons are emitted.



Mass of a neutron is 1.00867 amu (1.67493×10^{-24} g or 1.67493×10^{-27} kg)

3.4 PROPERTIES OF FUNDAMENTAL PARTICLES :

Atoms are made up-essentially, of three fundamental particles, which differ in mass and electric charge as follows :

	Electron	Proton	Neutron
Symbol	e or e ⁻	p	n
Approximate relative mass	1/1836	1	1
Approximate relative charge	-1	+1	0
Mass in kg	9.10939×10^{-31}	1.67262×10^{-27}	1.67493×10^{-27}
Mass in amu	0.00054	1.00727	1.00867
Actual charge/C	-1.6022×10^{-19}	$+1.6022 \times 10^{-19}$	0

Ex.1. Arrange the particle in their increasing order of specific charge ratio.

(a) e⁻, P, n, α-particle

(b) Na⁺, Li⁺, F⁻, Mg²⁺, Al³⁺

Sol. (a) $\left(\frac{e}{m}\right)_e = \frac{1e}{\left(\frac{1}{1836}\right)\text{amu}}$

$$\left(\frac{e}{m}\right)_p = \frac{1}{1} = 1 = \frac{1e}{1\text{amu}}$$

$$\left(\frac{e}{m}\right)_n = \frac{0}{1} = 0 = \frac{0e}{1\text{amu}}$$

$$\left(\frac{e}{m}\right)_\alpha = \frac{2}{4} = \frac{1}{2} = \frac{2e}{4\text{amu}}$$

Ans. $n < \alpha < p < e^-$

(b) $Na^+ = \frac{1}{23}$; $Li^+ = \frac{1}{7}$; $F^- = \frac{1}{19}$; $Mg^{2+} = \frac{2}{24} = \frac{1}{12}$; $Al^{3+} = \frac{3}{27} = \frac{1}{9}$
 $Na^+ < F^- < Mg^{2+} < Al^{3+} < Li^+$

Ex.2. Which of the following pairs have same specific charge $\left(\frac{e}{m}\right)$?

(a) electron & proton

(b) electron & positron

(c) proton & positron

(d) proton & deuteron

(e) α-particle & deuteron

Answer. b, e

Ex.3. Through what potential difference an α -particle should be accelerated to have speed 5×10^6 m/s.

Sol. : $qV = \frac{1}{2}mv^2$

$$(2 \times 1.6 \times 10^{-19} \times V) = \frac{1}{2} \times 4 \times 1.66 \times 10^{-27} \times (5 \times 10^6)^2$$

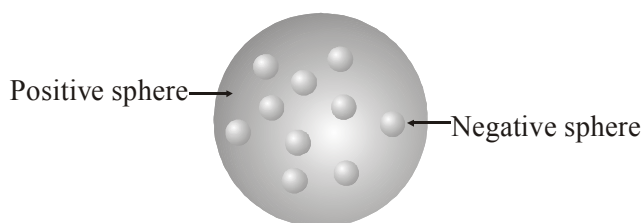
4. ATOMIC MODELS :

Observations obtained from the experiments mentioned in the previous sections have suggested that Dalton's indivisible atom is composed of sub-atomic particles carrying positive and negative charges. Different atomic models were proposed to explain the distributions of these charged particles in an atom. Although some of these models were not able to explain the stability of atoms, two of these models, proposed by J. J. Thomson and Ernest Rutherford are discussed below.

4.1 Thomson Model of Atom :

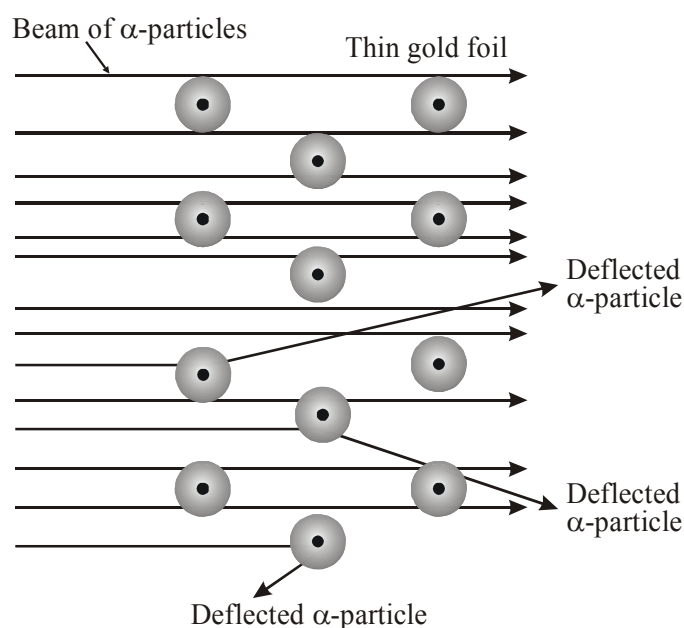
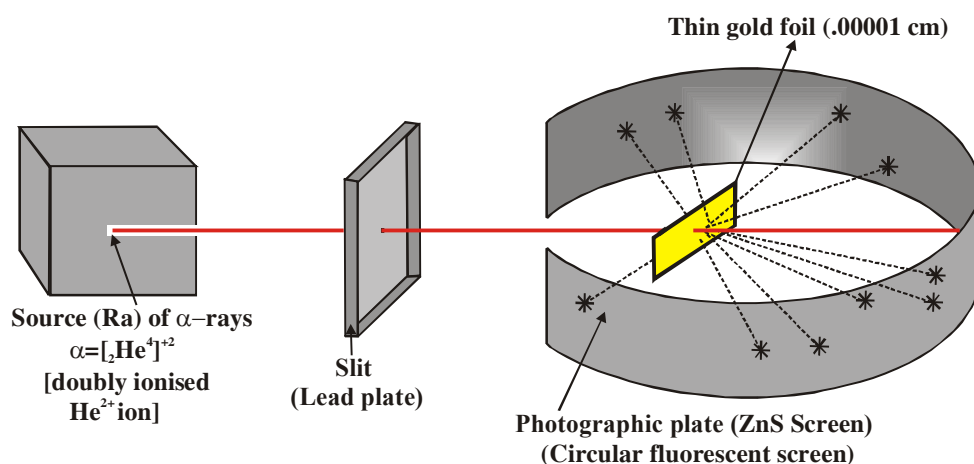
J. J. Thomson, in 1898, proposed that an atom possesses a spherical shape (radius approximately 10^{-10} m) in which the positive charge is uniformly distributed. The electrons are embedded into it in such a manner as to give the most stable electrostatic arrangement. Many different names are given to this model, **for example, plum pudding, raisin pudding or watermelon**. This model can be visualised as a pudding or watermelon of positive charge with plums or seeds (electrons) embedded into it. An important feature of this model is that the mass of the atom is assumed to be uniformly distributed over the atom. Although this model was able to explain the overall neutrality of the atom, but was not consistent with the results of later experiments.

Thomson was awarded Nobel Prize for physics in 1906, for his theoretical and experimental investigations on the conduction of electricity by gases.



Thomson model of atom

4.2 Rutherford's model :

Rutherford's α -scattering experiment

B. Schematic molecular view of the gold foil

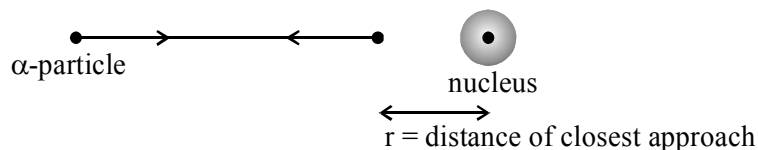
❖ Observations and conclusions :

- (i) Most of the α -particles passed through the gold foil undeflected. Hence, most of the space in the atom is empty.
- (ii) A small fraction of α -particles was deflected by small angles. A very few α -particles (~1 in 20,000) bounced back, that is, were deflected by nearly 180° .

The deflection must be due to enormous repulsive force showing that the positive charge of the atom is not spread throughout the atom as Thomson had presumed. The positive charge has to be concentrated in a very small volume that repelled and deflected the positively charged α -particles. Rutherford given the name **nucleus** to this positively charged center of atom.

- (iii) The volume occupied by the nucleus is negligibly small as compared to the total volume of atom. The radius of the atom is about 10^{-10} m, while that of nucleus is 10^{-15} m.

Rutherford estimated the size of nucleus by calculating the distance of closest approach.



The initial kinetic energy of α -particle must be equal to potential energy at distance of closest approach.

$$\text{K.E.} = \frac{1}{4\pi\epsilon_0} \cdot \frac{q_1 \cdot q_2}{r} = \frac{1}{4\pi\epsilon_0} \cdot \frac{(2e) \cdot (Ze)}{r}$$

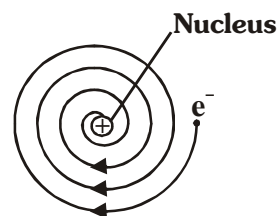
$$r = \frac{2Ze^2}{(4\pi\epsilon_0)(\text{K.E.})}$$

where Z = atomic number of element used in foil.

- (iv) Almost all mass of the atom is densely concentrated in extremely small region (nucleus).
 (v) The nucleus is surrounded by electrons that move around the nucleus with a very high speed in circular paths called orbits. Electrons and the nucleus are held together by electrostatic forces of attraction.

4.2.1 Drawbacks of Rutherford model :

- (i) According to the electromagnetic theory of Maxwell, charged particles when accelerated should emit electromagnetic radiation. Therefore, an electron in an orbit will emit radiation, the energy carried by radiation comes from electronic motion. The orbit will thus continue to shrink.



Calculations show that it should take an electron only 10^{-8} s to spiral into the nucleus. But this does not happen. Thus, the Rutherford model cannot explain the stability of an atom.

- (ii) It does not explain the arrangement of electrons revolving round nucleus.
 (iii) It does not explain the stability of nucleus against strong repulsive forces.
 (iv) It does not explain atomic spectrum.

Ex.4. An α -particles of kinetic energy of 5.4 MeV is projected towards gold nucleus. Calculate the distance of closet approach. (Atomic number of gold = 79, $1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$)

Sol : $\text{K.E.} = \frac{1}{4\pi\epsilon_0} \cdot \frac{q_1 q_2}{r}$

$$\text{or } 5.4 \times 10^6 \times 1.6 \times 10^{-19} = 9 \times 10^9 \times \frac{(2 \times 1.6 \times 10^{-19}) \times (79 \times 1.6 \times 10^{-19})}{r}$$

$$\therefore r = 4.21 \times 10^{-14} \text{ m}$$

Ex.5 An α -particles is projected towards the following nucleus with same kinetic energy in different experiement the distance of closet approach is maximum for

(A) Na ($Z = 11$)

(B) Ca ($Z = 20$)

(C) Ag ($Z = 47$)

(D) Au ($Z = 79$)

Answer. (A)

Ex.6. An α -particle, a proton, a deuteron and a neutron are projected towards the same nucleus with the same kinetic energy in different experiement. The distance of closet approach is minimum for

(A) α

(B) P

(C) d

(D) n

Answer. (D)

Ex.7 An α -particle having K.E. = 7.7 MeV is scattered by gold ($Z = 79$) nucleus through 180° . Find distance of closest approach.

$$\text{K.E.} = 7.7 \text{ MeV}$$

$$= 7.7 \times 10^6 \times 1.6 \times 10^{-19} \text{ J}$$

$$= 1.23 \times 10^{-12} \text{ J}$$

$$\frac{1}{4\pi\epsilon_0} = 9 \times 10^9 \text{ Nm}^2 \text{C}^{-2}$$

$$\text{Using we get : } \frac{9 \times 10^9 \times 2 \times 79 \times (1.6 \times 10^{-19})^2}{1.23 \times 10^{-12}}$$

$$r_0 = 3 \times 10^{-14} \text{ m}$$

From the above example it is clear that nuclear dimension cannot be greater than $3 \times 10^{-14} \text{ m}$.

5. WAVE THEORY :

A wave is defined as a periodic disturbance in space or in a medium that involves elastic displacement of material particles or a periodic change in some physical quantities such as T, P, V etc. Thus, wave motion represents propagation of a periodic disturbance carrying energy. The wave travels at right angles to the vibratory motion of the object.

When an object moves up and down or vibrates continuously, energy in the form of waves is transmitted by a vibrating object to a distant place. For example, when a stone is thrown in a still water of a pond, a disturbance is produced at a place where the stone strikes the water. This disturbance advances outwards in the same form and reaches the edges of the pond. Such a disturbance is called a **mechanical wave**.

The mechanical waves transmit only in a material medium. Besides the mechanical waves, there are waves which do not require any medium for their transmission. These waves are called *electromagnetic waves* or *electromagnetic radiations*.

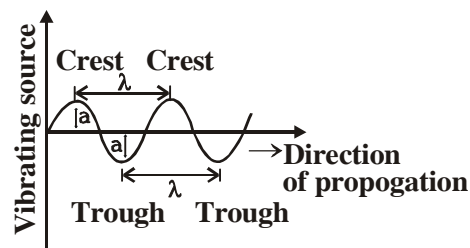
5.1 WAVE CHARACTERISTICS :

I. Wavelength (λ) :

It is defined as the distance between two nearest crests or nearest troughs.

It is measured in terms of a \AA (Angstrom), pm (Picometre), nm (nanometer), cm (centimetre), m (metre)

$$1 \text{ \AA} = 10^{-10} \text{ m}, \quad 1 \text{ pm} = 10^{-12} \text{ m}, \quad 1 \text{ nm} = 10^{-9} \text{ m}, \quad 1 \text{ cm} = 10^{-2} \text{ m}$$



II. Frequency (ν) :

Frequency of a wave is defined as the number of waves which pass through a point in 1 sec.

- It is measured in terms of Hertz (Hz), sec^{-1} , or cycle per second (cps)

$$1 \text{ Hertz} = 1 \text{ sec}^{-1}$$

III. Time period (T) : Time taken by a wave to pass through one point.

$$T = \frac{1}{\nu} \text{ sec.}$$

IV. Velocity (c) :

Velocity of a wave is defined as distance covered by a wave in 1 sec.

$$c = \lambda / T = \lambda \nu \quad \nu = c / \lambda \quad c = \nu (\text{sec}^{-1}) \times \lambda (\text{m}) \quad c = \nu \lambda (\text{m sec}^{-1})$$

Since c is constant for em-waves.

i.e. frequency is inversely proportional to λ

V. Wave number ($\bar{\nu}$) :

It is defined as number of waves per unit length. It is denoted by $\bar{\nu}$ & is expressed in cm^{-1} .

$$\lambda \text{ m} \rightarrow 1 \text{ wave}$$

$$1 \text{ m} \rightarrow 1/\lambda \text{ waves}$$

$$\bar{\nu} = \frac{1}{\lambda} \quad (1 \text{ cm}^{-1} = 100 \text{ m}^{-1})$$

- It is measured in terms of cm^{-1} , m^{-1} etc.

VI. Amplitude (a) :

It is the height of the crest or depth of the trough of a wave and is denoted by 'a'. It is half the vertical distance from the top of the wave to the bottom of the wave. It determines the intensity or brightness of the beam of light.

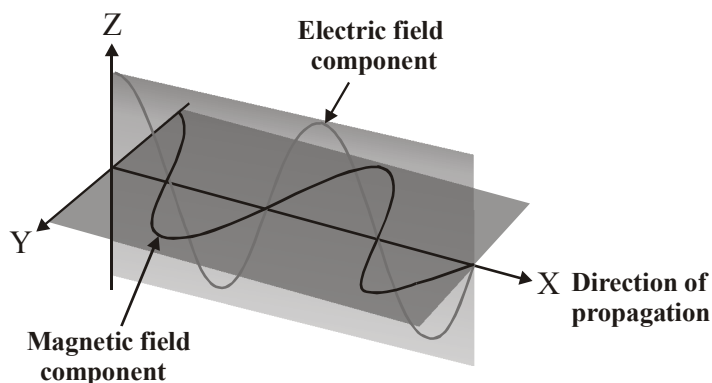
The amplitude of a wave in stretched string is the maximum displacement of the string from its normal position that of water waves is the maximum height of the water surface relative to its normal level, That of a sound wave is the maximum change in pressure relative to the normal pressure.

5.2 ELECTRO MAGNETIC (EM) WAVES :

James Maxwell (1870) suggested that when electrically charged particle moves under acceleration, alternating electrical and magnetic fields are produced and transmitted by it. These fields are transmitted in the forms of waves called electromagnetic waves or electromagnetic radiations.

❖ Main assumptions of Maxwell EM theory :

- (i) The oscillating electric and magnetic fields produced by oscillating charged particles are perpendicular to each other and both are perpendicular to the direction of propagation of the wave.



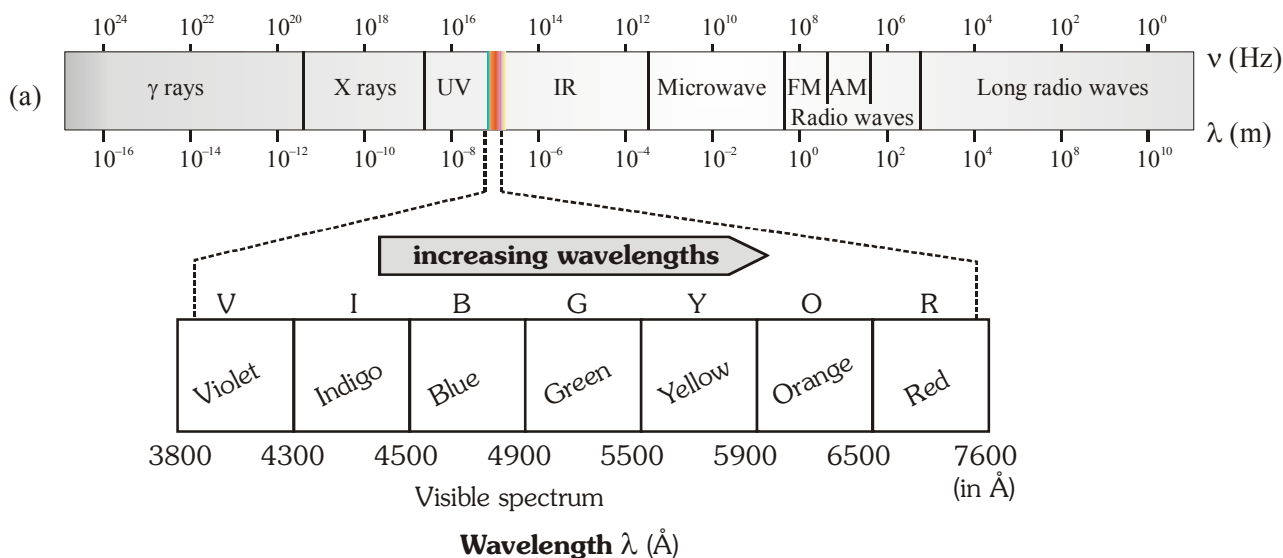
(The electric and magnetic field components of an electromagnetic wave. These components have the same wavelength, frequency, speed and amplitude, but they vibrate in two mutually perpendicular planes.)

- (ii) Unlike sound waves or water waves, electromagnetic waves do not require medium and can move in vacuum.
(However speed changes in different mediums)
- (iii) The EM waves travel with the velocity of light (3×10^8 m/sec) in vacuum.
- (iv) Energy of EM waves depends on its amplitude not on its frequency or wavelength.
(This assumptions was later proved to be wrong in some situations).

5.3 ELECTRO MAGNETIC SPECTRUM :

The arrangement of various types of electromagnetic radiations in the order of their increasing or decreasing wavelength or frequencies is known as electromagnetic spectrum. The wavelength decreases in the following order.

Radio waves > microwaves > Infrared > Television waves > Visible > Ultraviolet > X-rays > γ -rays
> cosmic rays



(a) The spectrum of electromagnetic radiation. (b) Visible spectrum. The visible region is only a small part of the entire spectrum.

Ex.8. Calculate the frequency of EMR (Electromagnetic radiation) of wave number 10^4 cm^{-1} .

$$\text{Sol: } v = \frac{c}{\lambda} = c\bar{\nu} = (3 \times 10^8 \text{ m/s})(10^4 \text{ cm}^{-1}) = (3 \times 10^{10} \text{ cm/s})(10^4 \text{ cm}^{-1}) = 3 \times 10^{14} \text{ Hz}.$$

Ex.9. A radio station radiate the radiowaves of frequency 20kHz. What is meter band of that radio station?

$$\text{Sol: } 20\text{kHz} = \frac{3 \times 10^8}{\lambda} \Rightarrow \lambda = 1.5 \times 10^4 \text{ m}$$

6. PARTICLE NATURE OF ELECTROMAGNETIC RADIATIONS

(PLANCK'S QUANTUM THEORY OF RADIATION)

Max Planck in 1901, put forward a theory known as "**Planck's Quantum Theory**". It regards electromagnetic radiations made up of particles. This was further extended by *Einstein* in 1905. The main points of the theory are :

- (i) The radiant energy is emitted or absorbed by atoms or molecules discontinuously in the form of small energy packets called quanta. In case of light, these energy packets are known as photons.
- (ii) The energy of each quantum is directly proportional to the frequency of the radiation i.e.

$$E \propto \nu \quad \text{or} \quad E = h\nu = \frac{hc}{\lambda}$$

Here h is a constant known as **Planck's constant**. Its value is 6.626×10^{-34} Joules sec.

- (iii) The total amount of energy emitted or absorbed by a body is some whole number multiple of quantum i.e.,

$$E = nh\nu \quad (\text{Here } n \text{ is a positive integer : } 1, 2, 3, 4 \dots \text{etc.})$$

Thus, Planck for the first time has given a relationship between the frequency (or wavelength) of the radiations and the energy associated with them. Cosmic rays, gamma rays and X-rays are high energy radiations since they have very high frequency. At the same time, microwaves and radiowaves with small frequency are regarded as low energy radiations.

❖ **Important features of Photon :**

- Source of energy (light) emits radiation in the form photons, which travel with speed of light.
- Energy of single photon, $E = h\nu = \frac{hc}{\lambda}$.
- All the photons in vacuum travel with speed 3×10^8 m/s but their speed is changed in different medium, however frequency remains same. Speed does not depend on energy.
- Photons travel as waves but are absorbed or emitted as particles.

Ex.10. Calculate the energy per quanta of an EMR of frequency 400 MHz.

Sol : $E = 6.626 \times 10^{-34} \times 4 \times 10^6 \text{ J/quanta}$

Ex.11. Calculate the energy per quanta of an EMR of wavelength 662.6 nm.

Sol : $E = n \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{662.6 \times 10^{-9} \text{ m}} = 3 \times 10^{-19} \text{ J/quanta}$

Ex.12. Calculate the wavelength (in Å) of an EMR of energy 3.1 eV/quanta.

Sol: $E = h\nu = h \frac{c}{\lambda} \Rightarrow E(\text{eV}) \times 1.602 \times 10^{-19} = \frac{1 \times 6.62 \times 10^{-34} \times 3 \times 10^8}{\lambda(\text{Å})}$

$$E(\text{eV}) \approx \frac{12400}{\lambda(\text{Å})} = \frac{1240}{\lambda(\text{nm})}$$

Ex.13. In order to see an object, 10^{-19} J must be received by our eyes. How many photons of green light must be received by our eyes for its visibility. ($\lambda = 550 \text{ nm}$, $h = 6.6 \times 10^{-34} \text{ J}$)

Sol : $E = n \frac{hc}{\lambda}$

$$10^{-19} = n \times \frac{6.6 \times 10^{-34} \times 3 \times 10^8}{5500 \times 10^{-9}}$$

$$n = \frac{5}{18} \approx 1$$

Ex.14. A bulb is rated as 110 watt. If it emits 25% of absorbed energy as red light ($\lambda = 6626\text{\AA}$), how many photons are emitted out by the bulb per second.

Sol: $110 \times \frac{25}{100} = n \times \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{6626 \times 10^{-10}}$

Ex.15. The wavelength of microwave radiation is 0.08 m. How many moles of photons is needed to increase the temperature of 400 gm water from 25° to 45°C, assuming 25% efficiency.

Specific heat capacity = 4.2 J/K-gm

Sol: $\left(\frac{nhc}{\lambda} \right) \times \frac{25}{100} = ms\Delta t$

$$n \times \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{0.08} \times \frac{25}{100} = 400 \times 4.2 \times 20$$

$$\therefore \text{Number of moles of photon} = \frac{n}{N_A}$$

Ex.16. A dye absorbs the radiation of 4000 Å and fluoresces the radiation of 5000 Å. If only 40% of the absorbed energy is emitted out, calculate the ratio of number of quanta emitted out and the number of quanta absorbed.

Sol: $E_a \times \frac{40}{100} = E_e$

$$n_a \times \frac{hc}{4000\text{\AA}} \times \frac{40}{100} = n_e \times \frac{hc}{5000\text{\AA}}$$

$$\frac{n_e}{n_a} = \frac{40}{100} \times \frac{5000}{4000} = \frac{1}{2}$$

Ex.17. The bond dissociation energy of Cl–Cl bond in chlorine gas is 240 kJ/mol. Calculate the longest wavelength of EMR needed to dissociate bond. Assume one photon may dissociate only one bond.

Sol: $\frac{240 \times 10^3}{6 \times 10^{23}} = \frac{1 \times 6.626 \times 10^{-34} \times 3 \times 10^8}{\lambda}$

Ex.18 A near ultra violet photon of wavelength 300 nm is absorbed by a gas and then emitted as two photons. One photon is of red light with wavelength 760 nm. What would be the wave length of the second photon ?

Sol. It may noted that energy of photon which adsorbed is emitted as sum of the energy of two photons.

$$\text{Energy absorbed } h\nu = \frac{hc}{\lambda}$$

According to available information,

$$\frac{hc}{\lambda} = \frac{hc}{\lambda_1} + \frac{hc}{\lambda_2}; \frac{1}{\lambda} = \frac{1}{\lambda_1} + \frac{1}{\lambda_2}; \frac{1}{\lambda_2} = \left[\frac{1}{\lambda} - \frac{1}{\lambda_1} \right]$$

Now, $\lambda = 300 \text{ nm}$; $\lambda_1 = 760 \text{ nm}$; λ_2 can be calculated as :

$$\frac{1}{\lambda_2} = \left[\frac{1}{300} - \frac{1}{760} \right] = \frac{760 - 300}{300 \times 760} (\text{nm}^{-1})$$

$$\frac{1}{\lambda_2} = \frac{460}{760 \times 300} (\text{nm}^{-1})$$

or $\lambda_2 = 496 \text{ nm}$

7. PHOTOELECTRIC EFFECT :

Hertz in **1887** observed that when a light of certain frequency strikes the surface of a metal, electrons are ejected from the metal. This phenomenon is known as **photoelectric effect** and the ejected **electrons** are called **photoelectrons**.

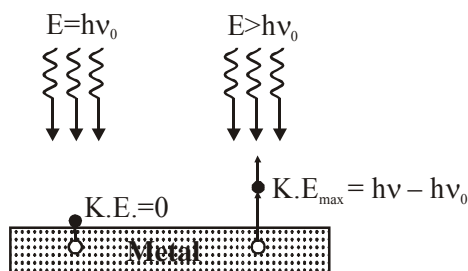
A few metals, which are having low ionisation energy like Cesium, show this effect under the action of visible light but many more show it under the action of more energetic ultraviolet light.

7.1 The experimental findings are summarized as below :

- Electrons come out as soon as the light (of sufficient energy) strikes the metal surface. There is no time lag between the two events.
- The light of any frequency will not be able to cause ejection of electrons from a metal surface. There is a minimum frequency, called the **threshold (or critical) frequency**, which can just cause the ejection. This frequency varies with the nature of the metal. The higher the frequency of the light, the more energy the photoelectrons have. Blue light results in faster electrons than red light.
- Photoelectric current is increased with increase in intensity of light of same frequency, if emission is permitted, i.e. a bright light yields more photoelectrons than a dim one of the same frequency, but the electron energies remain the same.

7.2 Einstein's explanation :

Light must have stream of energy particles or quanta of energy ($h\nu$). Suppose, the threshold frequency of light required for ejecting electrons from a metal is ν_0 , when a photon of light of this frequency strikes a metal it imparts its entire energy ($h\nu_0$) to the electron.



This energy enables the electron to break away from the surface by overcoming the attractive influence of the nucleus. Thus each photon can eject one electron. If the frequency of light is less than ν_0 , there is no ejection of electron. If the frequency of light is higher than ν_0 (let it be ν), the photon of this light having higher energy ($h\nu$), will impart some energy to the electron that

is needed to remove it away from the atom. Einstein proposed that light consisted of quanta, which we call photons with a frequency over a certain threshold would have sufficient energy to eject a single electron, producing the photoelectric effect.

7.3 Einstein's Equation for the Photoelectric Effect :

Einstein's interpretation of the photoelectric effect results in equation :

Energy of photon = Energy needed to remove an electron + Max. Kinetic energy of the emitted electron

The excess energy would give a certain velocity (i.e. kinetic energy) to the electron.

$$h\nu = h\nu_0 + K.E._{max.}$$

$$h\nu = h\nu_0 + \frac{1}{2}mv^2$$

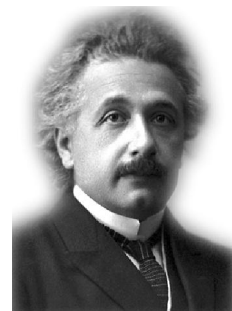
$$\frac{1}{2}mv^2 = h\nu - h\nu_0$$

where ν = frequency of the incident light, ν_0 = threshold frequency

v = max. speed of photoelectron.

$h\nu_0$ is the **threshold energy** (or) the **work function** denoted by $\phi = h\nu_0$ (minimum energy of the photon to liberate electron). It is constant for particular metal.

The maximum kinetic energy of the photoelectrons increases linearly with the frequency of incident light. This, if the energy of the ejected electrons is plotted as a function of frequency, it results in a straight line whose slope is equal to Planck's constant 'h' and whose intercept is $h\nu_0$.



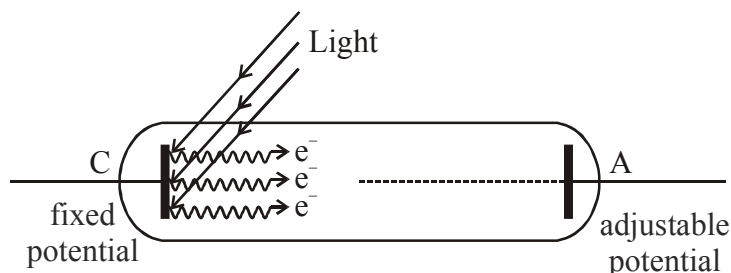
Albert Einstein (1879 - 1955)

Albert Einstein, a German born American physicist, is regarded by many as one of the two great physicists the world has known (the other is Isaac Newton). His three research papers (on special relativity, Brownian motion and the photoelectric effect) which he published in 1905, **Albert Einstein (1879 - 1955)** while he was employed as a technical assistant in a Swiss patent office in Berne have profoundly influenced the development of physics. He received the Nobel Prize in Physics in 1921 for his explanation of the photoelectric effect.

7.4 Important conclusions from photoelectric effect :

- (i) Photoelectric effect demonstrates particle nature of radiation.
- (ii) A photon is quanta of energy. Its rest mass is zero. This is why photon can give up its all energy to the particle it strikes.
- (iii) There is no effect of frequency of incident light on the number of the emitted photoelectrons.
- (iv) There is no effect of intensity of incident light on the K.E. of the emitted photoelectrons.

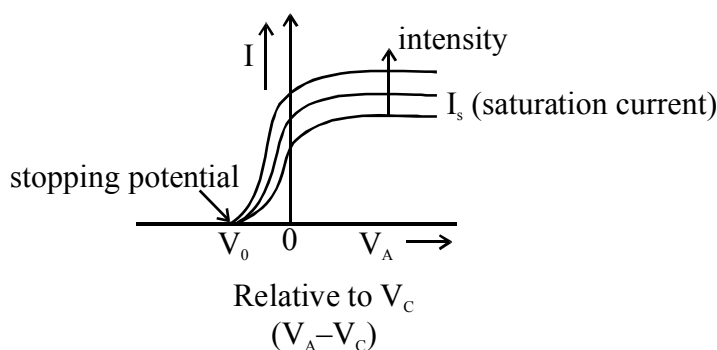
7.5 SATURATION CURRENT & STOPPING POTENTIAL



Case-I : $V_C = V_A$
Some of the ejected electrons reach at electrode A resulting photocurrent.

Case-II : $V_C < V_A$
As electrode (A) is at high potential it attracts the electron & even a slower electron will reach at electrode A. It will result in increase in photocurrent. Further increase in the potential difference, a situation may result when the slowest photocurrent electron reach at electrode. It results maximum called **saturation current**. Further increase in potential will not increase photocurrent.

Case-III : $V_C > V_A$
As electrode (A) is at low potential. It will repel electron resulting decrease in photocurrent. Further decrease in potential at electrode (A) may result a situation when the fastest electron just fails to reach at (A) and the photocurrent drops to zero. The potential of (A) relative to C to just stop photocurrent is called **stopping potential**.



On increasing the intensity of light the stopping potential does not change because the maximum K.E. of photoelectron does not change. But the photocurrent increases, because the number of photon falling on the surface increase.

If the frequency of light is changed, the stopping potential will change.

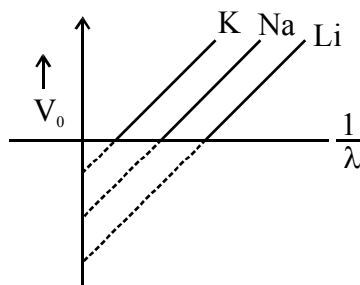
$$(KE)_{\max} = eV_0$$

$$(KE)_{\max} = h\nu - h\nu_0$$

$$eV_0 = \frac{hc}{\lambda} - \phi$$

$$V_0 = \frac{hc}{e} \frac{1}{\lambda} - \frac{\phi}{e}$$

y x



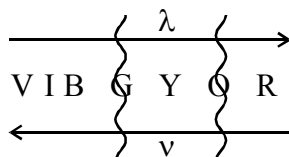
Ex.19. From a metal surface, photoelectron never comes out by orange light but comes from green light. Predict about the injection of photoelectron from the same metal by

(i) Red (ii) Blue (iii) Yellow light

Sol: (i) Red light = No

(ii) Blue light = Yes

(iii) Yellow light = Can't say



Ex.20. The work function of a metal is 3 eV. If EMR of 200 nm fall on the metal surface, calculate the maximum speed of photoelectron ejected.

Sol: $E = \frac{1240}{200} = 6.2 \text{ eV}$

$$(KE)_{\max} = h\nu - \phi$$

$$\frac{1}{2}mv^2 = (6.2 - 3) \text{ eV}$$

$$\frac{1}{2} \times 9.1 \times 10^{-31} v_{\max}^2 = 3.2 \times 1.6 \times 10^{-19}$$

Ex.21. When EMR of frequency $5 \times 10^{15} \text{ Hz}$ fall on a metal surface, the maximum kinetic energy of photoelectron is double than the photoelectron which emits when EMR of frequency $3 \times 10^{15} \text{ Hz}$ fall on the same metal. The threshold frequency for the metal is

Sol: $(K.E.)_1 = h \times 5 \times 10^{15} - h\nu_0$

$$(K.E.)_2 = h \times 3 \times 10^{15} - h\nu_0$$

$$2E_1 = E_2$$

$$\nu_0 = 1 \times 10^{15} \text{ Hz.}$$

Ex.22 A photon of wavelength 3000 \AA strikes a metal surface, the work function of the metal being 2.20 eV . Calculate (i) the energy of the photon in eV (ii) the kinetic energy of the emitted photo electron and (iii) the velocity of the photo electron.

Sol. (i) Energy of the photon

$$E = h\nu = \frac{hc}{\lambda} = \frac{(6.6 \times 10^{-34} \text{ Js})(3 \times 10^8 \text{ ms}^{-1})}{3 \times 10^{-7} \text{ m}} = 6.6 \times 10^{-19} \text{ J}$$

$$1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$$

$$\text{Therefore } E = \frac{6.6 \times 10^{-19} \text{ J}}{1.6 \times 10^{-19} \text{ J/eV}} = 4.125 \text{ eV}$$

(ii) Kinetic energy of the emitted photo electron

$$\text{Work function} = 2.20 \text{ eV}$$

$$\text{Therefore, KE} = 4.125 - 2.20$$

$$= 1.925 \text{ eV} = 3.08 \times 10^{-19} \text{ J}$$

(iii) Velocity of the photo electron

$$\text{KE} = \frac{1}{2}mv^2 = 3.08 \times 10^{-19} \text{ J}$$

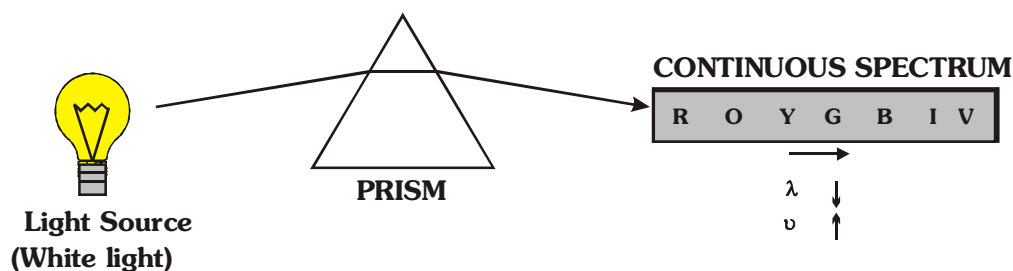
$$\text{Therefore, velocity (v)} = \sqrt{\frac{2 \times 3.08 \times 10^{-19}}{9.1 \times 10^{-31}}} = 8.22 \times 10^5 \text{ ms}^{-1}$$

8. SPECTRUM

It is the impressions produced on any screen when a light falls on it after passing through prism or prism like material.

Classification of spectrum :

- (i) **Continuous and discontinuous spectrum :** In continuous spectrum, the impression produced on screen overlap each other, but in discontinuous spectrum, same gap exist between the impression. The spectrum of white light that we can see ranges from violet at $7.50 \times 10^{14} \text{ Hz}$ to red at $4 \times 10^{14} \text{ Hz}$. This spectrum is called *continuous spectrum* because violet merges into blue, blue into green, and so on. A similar spectrum is produced when a rainbow forms in the sky. In a continuous spectrum, radiations corresponding to all the wavelengths are present.



- (ii) **Emission and Absorption Spectra :** The spectrum of radiation emitted by a substance that has absorbed energy is called an **emission spectrum**. Atoms, molecules or ions that have absorbed radiation are said to be '**excited**'. To produce an emission spectrum, energy is supplied to a sample by heating it or irradiating it and the wavelength (or frequency) of the radiation emitted, as the sample gives up the absorbed energy, is recorded.

An absorption spectrum is like the photographic negative of an emission spectrum. A continuum of radiation is passed through a sample which absorbs radiation of certain wavelengths. The missing wavelength which corresponds to the radiation absorbed by the matter, leave dark spaces in the bright continuous spectrum.

The study of emission or absorption spectra is referred to as **spectroscopy**. The spectrum of the visible light, as discussed above, was continuous as all wavelengths (red to violet) of the visible light are represented in the spectra. The emission spectra of atoms in the gas phase, on the other hand, do not show a continuous spread of wavelength from red to violet, rather they emit light only at specific wavelengths with dark spaces between them. Such spectra are called **line spectra** or **atomic spectra** because the emitted radiation is identified by the appearance of bright lines in the spectra (Fig)

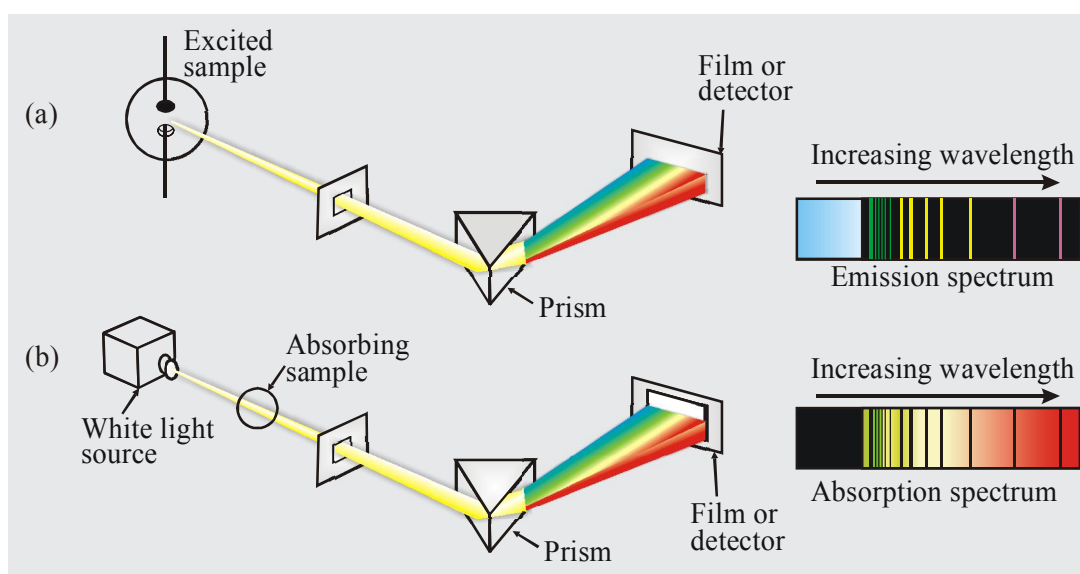


Fig. (a) Atomic emission. The light emitted by a sample of excited hydrogen atoms (or any other element) can be passed through a prism and separated into certain discrete wavelengths. Thus an emission spectrum, which is a photographic recording of the separated wavelengths is called as line spectrum. Any sample of reasonable size contains an enormous number of atoms. Although a single atom can be in only one excited state at a time, the collection of atoms contains all possible excited states. The light emitted as these atoms fall to lower energy states is responsible for the spectrum. **(b) Atomic absorption.** When white light is passed through unexcited atomic hydrogen and then through a slit and prism, the transmitted light is lacking in intensity at the same wavelengths as are emitted in (a) The recorded absorption spectrum is also a line spectrum and the photographic negative of the emission spectrum.

Line emission spectra are of great interest in the study of electronic structure. Each element has a unique line emission spectrum. The characteristic lines in atomic spectra can be used in chemical analysis to identify unknown atoms in the same way as finger prints are used to identify people. The exact matching of lines of the emission spectrum of the atoms of a known element with the lines from an unknown sample quickly establishes the identity of the latter, German chemist, Robert Bunsen (1811-1899) was one of the first investigators to use line spectra to identify elements. Elements like rubidium (Rb), caesium (Cs), thallium (Tl), indium (In), gallium (Ga) and scandium (Sc) were discovered when their minerals were analysed by spectroscopic methods. The element helium (He) was discovered in the sun by spectroscopic method.

9. BOHR'S ATOMIC MODEL

Bohr's model for hydrogen atom is based on the following postulates:

- (i) The electron in the hydrogen atom can move around the nucleus in a circular path of fixed radius and energy. These paths are called **orbits**, stationary states or allowed energy states. These orbits are arranged concentrically around the nucleus.
- (ii) The energy of an electron in the orbit does not change with time. However, the electron will move from a lower stationary state to a higher stationary state when required amount of energy is absorbed by the electron or energy is emitted when electron moves from higher stationary state to lower stationary state. The energy change does not take place in a continuous manner.
- (iii) The frequency of radiation absorbed or emitted when transition occurs between two stationary states that differ in energy by ΔE , is given by :

$$\nu = \frac{\Delta E}{h} = \frac{E_2 - E_1}{h}$$

Where E_1 and E_2 are the energies of the lower and higher allowed energy states respectively. This expression is commonly known as Bohr's frequency rule.

- (iv) The angular momentum of an electron in a given stationary state can be expressed as in equation

$$m_e v r = n \cdot \frac{h}{2\pi} \quad n = 1, 2, 3$$

Thus an electron can move only in those orbits for which its angular momentum is integral multiple of $h/2\pi$ that is why only certain fixed orbits are allowed.

9.1 APPLICATION OF BOHR'S MODEL

When electron revolves in fixed circular orbit then electrostatic force of attraction and centrifugal force are equal.

$$\text{Electrostatic force} = \frac{K q_1 q_2}{r^2} = \frac{K \cdot Ze \cdot e}{r^2} = \frac{KZe^2}{r^2}$$

Where, constant $K = 9 \times 10^9 \text{ Nm}^2/\text{C}^2$ (MKS) = 1 (CGS)



Niels Bohr
(1885-1962)

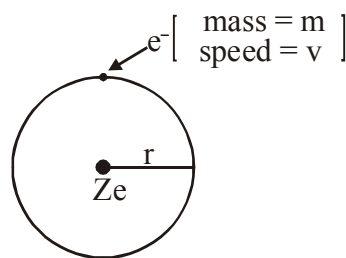
Niels Bohr, was a Danish physicist. After first world war, Bohr worked for peaceful uses of atomic energy. He was awarded the Nobel Prize in physics in 1922.

$$\text{Centrifugal force} = \frac{mv^2}{r}$$

In balanced condition

Electrostatic force = Centrifugal force

$$\frac{KZe^2}{r^2} = \frac{mv^2}{r} \text{ or } \frac{KZe^2}{r} = mv^2 \text{ or } \frac{Ze^2}{r} = mv^2 \text{ (CGS)(i)}$$



9.1.1 Radius of various orbits (shell) :

According to Bohr model, $mvr = \frac{nh}{2\pi}$

$$v = \frac{nh}{2\pi mr} \text{(ii)}$$

Now putting the value of v from eq.(ii) into eq.(i)

$$\frac{KZe^2}{r} = m \left(\frac{nh}{2\pi mr} \right)^2$$

$$\frac{KZe^2}{r} = \frac{mn^2h^2}{4\pi^2m^2r^2}$$

$$r = \frac{n^2h^2}{4\pi^2mKZe^2} \text{ or } r = \frac{n^2h^2}{4\pi^2mZe^2} \text{ (CGS } \because K=1) \text{(iii)}$$

Putting the value of π , h , m , K , & e (Constants) in the above eq. (iii)

$$r = 0.529 \times 10^{-10} \times \frac{n^2}{Z} \text{ m} \quad \{ \text{\AA} = 10^{-10} \text{ m} = 10^{-8} \text{ cm} \}$$

$$\text{or } \boxed{r_n = 0.529 \times \frac{n^2}{Z} \text{\AA}}$$

This formula is only applicable for hydrogen and hydrogen like species i.e. species containing single electron.

9.1.2. Velocity of electron in Bohr orbit :

According to Bohr postulate

$$mvr = \frac{nh}{2\pi}$$

$$v = \frac{nh}{2\pi mr} = \frac{nh}{\frac{2\pi m \times n^2 h^2}{4\pi^2 m K Z e^2}}$$

$$v = \frac{2\pi K Z e^2}{nh} \text{ (MKS)(iv)}$$

$$v = \frac{2\pi Z e^2}{nh} \text{ (CGS)}$$

Putting the value of π , h , K , & e (Constants) in the above eq (iv)

$$v = 2.18 \times 10^6 \frac{Z}{n} \text{ m/s}$$

9.1.3. Total energy of electron in Bohr orbit :

Total energy of an electron is the sum of kinetic and potential energy.

i.e. $T.E. = K.E. + P.E.$

(i) Potential energy : $P.E. = -\frac{Kq_1q_2}{r} = -\frac{KZe^2}{r} = -\frac{KZe^2}{r}$

(ii) Kinetic energy : $K.E. = \frac{1}{2}mv^2$

But $\frac{KZe^2}{r} = mv^2$ (By eq. i)

$K.E. = \frac{KZe^2}{2r}$

(iii) Total energy : $T.E. = K.E. + P.E.$

$T.E. = \frac{KZe^2}{2r} - \frac{KZe^2}{r} = -\frac{KZe^2}{2r}$

Now putting the value of r from eq. (iii)

$T.E. = -\frac{KZe^2 \times 4\pi^2 m KZe^2}{2n^2 h^2} \Rightarrow -\frac{2\pi^2 m \times K^2 Z^2 e^4}{n^2 h^2}$

Now putting the value of π , K , e , m , h , we get :

$T.E. = -2.18 \times 10^{-18} \times \frac{Z^2}{n^2} \text{ J / atom} = -1312 \times \frac{Z^2}{n^2} \text{ kJ/mol}$

$= -2.18 \times 10^{-11} \times \frac{Z^2}{n^2} \text{ erg/atom} = -313.6 \times \frac{Z^2}{n^2} \text{ Kcal/mol}$

$= -13.6 \times \frac{Z^2}{n^2} \text{ eV/atom} \Rightarrow E_n = -\frac{13.6Z^2}{n^2} \text{ eV/atom}$

9.1.4 Some extra points :

(i) $K.E. = \frac{KZe^2}{2r}$ i.e. $K.E. \propto \frac{1}{r}$ On increasing radius, K.E. decreases.

(ii) $P.E. = -\frac{KZe^2}{r}$ i.e. $P.E. \propto -\frac{1}{r}$ On increasing radius, P.E. increases.

(iii) $T.E. = -\frac{KZe^2}{2r}$ i.e. $E \propto -\frac{1}{r}$ On increasing radius, total energy increases.

(iv) Relation between T.E., P.E. and K.E.

$P.E. = -2 KE$

$KE = -T.E.$

$P.E. = 2 T.E.$

Ex.26 Calculate the energy of Li^{+2} atom for 2nd excited state.

Sol. $E = -13.6 \times \frac{Z^2}{n^2}$

$\therefore Z = 3$ and e^- exist in 2nd excited state, means e^- present in 3rd shell i.e. $n = 3$

$$\therefore E = -13.6 \times \frac{(3)^2}{(3)^2} = -13.6 \text{ eV/atom}$$

Ex.27 If the P.E. of an electron is -6.8 eV in hydrogen atom then find out K.E., E of orbit where electron exist & radius of orbit.

Sol. (i). P.E. = -2K.E.

$$-6.8 = -2\text{K.E.}$$

$$\frac{6.8}{2} = \text{K.E.} \quad \text{K.E.} = 3.4 \text{ eV}$$

(ii). $E = -\text{K.E.}$
 $= -3.4 \text{ eV}$

(iii). Orbit = 2nd

$$\therefore E = -13.6 \times \frac{Z^2}{n^2}$$

$$\therefore 3.4 = -13.6 \times \frac{1^2}{n^2}$$

$$\Rightarrow n^2 = \frac{-13.6}{-3.4} = 4$$

$$\text{i.e. } n = 2$$

(iv). $r = 0.529 \times \frac{n^2}{Z} \text{ \AA}$

$$r = 0.529 \times \frac{(2)^2}{1} \text{ \AA}$$

$$= 0.529 \times 4 \text{ \AA} = 2.16 \text{ \AA}$$

Ex.28 The ionization energy for the hydrogen atom is 13.6 eV then calculate the required energy in eV to excite it from the ground state to 1st excited state.

Sol. Ionization energy = 13.6 eV

i.e. 1st energy state = -13.6 eV

Energy of 1st excited state

i.e. 2nd orbit = -3.4 eV

so, $E_2 - E_1 = -3.4 + 13.6 = 10.2 \text{ eV}$

Ex.29 Calculate the amount of energy absorbed in the transition $n = 1$ to $n = 3$ in Li^{2+} ion.

Sol. n_1 orbit \longleftrightarrow n_2 orbit

$$\Delta E = E_{n_2} - E_{n_1} = \left(-13.6 \frac{Z_1^2}{n_2^2} \right) - \left(-13.6 \frac{Z_2^2}{n_1^2} \right)$$

$$\Delta E = 13.6 Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{eV}$$

$$\Delta E = 13.6 \times 3^2 \left(\frac{1}{1^2} - \frac{1}{3^2} \right) = 108.8 \text{eV}$$

Ex.30 Calculate the excitation energy of Be^{3+} ion in ground state.

Sol. $\Delta E = 13.6 \times 16 \left(\frac{1}{1} - \frac{1}{4} \right) = 163.2 \text{ eV}$

Ex.31 The ionisation energy of He^+ ion is x kJ/mole. Calculate ionisation energy of Li^{2+} ion.

Sol. For I.E. $\Rightarrow n = 1 \longrightarrow n = \infty$

$$IE = 13.6 Z^2 \left(\frac{1}{1^2} - \frac{1}{\infty^2} \right) = 13.6 Z^2 \text{ eV}$$

$$\frac{(IE.)_{\text{Li}^{2+}}}{(IE.)_{\text{He}^+}} = \frac{3^2}{2^2} \Rightarrow (IE.)_{\text{Li}^{2+}} = \frac{9}{4} x \text{ kJ/mol}$$

Ex.32 The ionisation energy for a single electron system is 14.4 eV. Calculate the amount of energy released when electron jumps from 3rd orbits to 2nd orbit.

Sol. $\Delta E = (IE) \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = 14.4 \times \left(\frac{1}{4} - \frac{1}{9} \right) = 2 \text{ eV}$

Ex.33 Calculate the speed of an electron in the 3rd orbit of the Li^{2+} ion. Also calculate the number of revolutions per second that it makes around the nucleus.

Sol. Radius of 2nd orbit $= r_1 \times \frac{(n)^2}{Z} = 0.529 \times \frac{(3)^2}{3} = 1.587 \text{\AA}$

Velocity of electron in 2nd orbit, $v = 2.18 \times 10^6 \frac{Z}{n} \text{ m/sec} = 2.18 \times 10^6 \text{ m/sec}$

$$\begin{aligned} \text{No. of revolutions/sec} &= \frac{1}{2\pi r / v} = \frac{v}{2\pi r} = \frac{2.18 \times 10^6 \text{ m/sec}}{2 \times 3.14 \times 1.587 \times 10^{-10} \text{ m}} \\ &= 2.187 \times 10^{15} \text{ rev/sec} \end{aligned}$$

9.2 RYDBERG FORMULA

If an electron shows transition from n_2 to n_1 energy level then energy change ΔE will be.

$$\Delta E = E_{n_2} - E_{n_1}$$

$$\Delta E = \frac{-2\pi^2 m K^2 Z^2 e^4}{n_2^2 h^2} - \left[\frac{-2\pi^2 m K^2 Z^2 e^4}{n_1^2 h^2} \right] = \frac{2\pi^2 m K^2 Z^2 e^4}{n_1^2 h^2} - \frac{2\pi^2 m K^2 Z^2 e^4}{n_2^2 h^2}$$

But $\Delta E = h\nu = \frac{hc}{\lambda}$

$$\therefore \frac{hc}{\lambda} = \frac{2\pi^2 m K^2 Z^2 e^4}{h^2} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

$$\frac{1}{\lambda} = \frac{2\pi^2 m K^2 e^4 Z^2}{ch^3} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

where $\frac{2\pi^2 m K^2 e^4}{ch^3}$ is a constant called Rydberg constant (R) (Assume nucleus is stationary)

$$\text{So, } \bar{\nu} = \frac{1}{\lambda} = RZ^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

$$\text{value of } R = 109677 \text{ cm}^{-1} = 10967700 \text{ m}^{-1} \\ \approx 109700 \text{ cm}^{-1} \approx 10970000 \text{ m}^{-1}$$

$$\frac{1}{R} = 912 \text{ \AA}$$

Ex.34 What is the wavelength of light emitted when the electron in a hydrogen atom undergoes transition from the energy level with $n = 4$ to the energy level with $n = 1$?

Sol. According to Rydberg's formula, $\bar{\nu}(\text{cm}^{-1}) = 109,677 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$

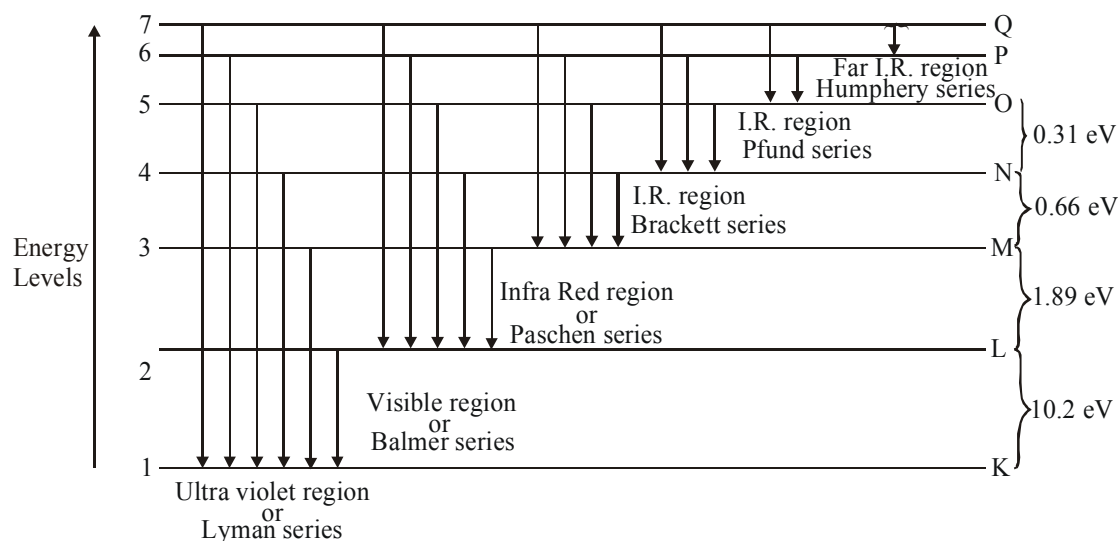
In the present case $n_2 = 4$ and $n_1 = 1$

$$\bar{\nu} = 109,677 \left(\frac{1}{(1)^2} - \frac{1}{(4)^2} \right) = 109,677 \times \frac{15}{16} = 102822 \text{ cm}^{-1}$$

$$\lambda = \frac{1}{\bar{\nu}} = \frac{1}{102822} \text{ cm} = 9.7 \times 10^{-6} \text{ cm} = 9.7 \times 10^{-6} \times 10^7 \text{ nm} = \mathbf{97 \text{ nm.}}$$

9.3 HYDROGEN LINE SPECTRUM :

When an electric excitation is applied on atomic hydrogen gas at low pressure, a bluish light is emitted. When a ray of this light is passed through a prism, a spectrum of several isolated sharp lines is obtained. The wavelength of various lines show that spectrum lines lie in visible, Ultraviolet and Infra red region. These lines are grouped into different series.



Series	Discovered by	Regions	n_2	n_1
Lyman	Lyman	U.V. region	$n_2 = 2, 3, 4 \dots$	$n_1 = 1$
Balmer	Balmer	Visible region	$n_2 = 3, 4, 5 \dots$	$n_1 = 2$
Paschen	Paschen	Infra red (I.R.)	$n_2 = 4, 5, 6 \dots$	$n_1 = 3$
Brackett	Brackett	I.R. region	$n_2 = 5, 6, 7 \dots$	$n_1 = 4$
Pfund	Pfund	I.R. region	$n_2 = 6, 7, 8 \dots$	$n_1 = 5$
Humphery	Humphery	Far I.R. region	$n_2 = 7, 8, 9 \dots$	$n_1 = 6$

□ **KEY POINTS :**

- First line / Starting line / Initial line ($\lambda_{\max.}$ and $\nu_{\min.}$)
- Last line / limiting line / Series limit ($\lambda_{\min.}$ and $\nu_{\max.}$)
- First line of any series = α line
Second line of any series = β line
Third line of any series = γ line
- Total no. of emission lines between n_2 & $n_1 = \frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$, ($n_2 > n_1$)
- For transition from any orbit 'n' to $n = 1$, total no. of emission lines = $\frac{n(n-1)}{2}$

Ex.35 In a hydrogen spectrum if electron moves from 6^{th} to 2^{nd} by transition in multi steps then find out the number of lines in spectrum

Sol. Total number of line = $4 + 3 + 2 + 1 + 0 = 10$

$$\text{Total number of lines} = \frac{(n_2 - n_1)[(n_2 - n_1) + 1]}{2} = \frac{(6 - 2)(4 + 1)}{2} = 10$$

Ex.36 In the spectrum of He^+ ion the wavelength of α line of Balmer series is $x \text{ \AA}$. What is the wavelength of α line of Paschen series.

Sol. $\frac{1}{\lambda_1} = RZ^2 \left(\frac{1}{2^2} - \frac{1}{3^2} \right)$

$$\frac{1}{\lambda_2} = RZ^2 \left(\frac{1}{3^2} - \frac{1}{5^2} \right)$$

$$\frac{\lambda_2}{\lambda_1} = \frac{\frac{1}{2^2} - \frac{1}{3^2}}{\frac{1}{3^2} - \frac{1}{5^2}} \Rightarrow \frac{\lambda_2}{x \text{ \AA}} = \frac{5}{16} \times \frac{25}{4}$$

Ex.37 A sample of He^+ ions in ground state absorbs the radiation of $x \text{ \AA}$. subsequently, the sample emit radiation of 6 different wavelength. Calculate the value of x .

Sol.
$$\frac{1}{x} = R \left(\frac{1}{1^2} - \frac{1}{4^2} \right) \times 2^2$$
$$x = \frac{16}{15} \times \frac{912}{4} \text{ \AA}$$

Ex.38 In a hydrogen spectrum if electron moves from 6^{th} to 2^{nd} by transition in multi steps then find out the number of lines in spectrum

Sol. Total number of line = $4 + 3 + 2 + 1 + 0$
= 10

$$\text{Total number of lines} = \frac{(n_2 - n_1)[(n_2 - n_1) + 1]}{2} = \frac{(6 - 2)(4 + 1)}{2} \Rightarrow \frac{4 \times 5}{2} = 10$$

9.4 Limitation of the Bohr's model

- Bohr's theory does not explain the spectrum of multi electron atom.
- Why the Angular momentum of the revolving electron is equal to $\frac{nh}{2\pi}$, has not been explained by Bohr's theory.
- Bohr inter-related quantum theory of radiation and classical law of physics without any theoretical explanation. This was the biggest drawback of this model.
- Bohr's theory does not explain the fine structure of spectral lines. Fine structure of the spectral line is obtained when spectrum is viewed by a spectroscopy of high resolving power.
- Bohr's theory does not explain the splitting of spectral lines in the presence of magnetic field (**Zeeman effect**) or electric field (**Stark effect**)

10. DUAL BEHAVIOUR OF MATTER & DE BROGLIE WAVELENGTH :

In 1923, a French physicist, **Louis de Broglie** suggested

that, like light, matter also has dual character. It exhibits wave as well as particle nature. According to de Broglie, the wavelength λ of an electron is inversely proportional to its momentum p .

$$\lambda \propto \frac{1}{p} \quad \text{or} \quad \lambda \propto \frac{1}{mv}$$

$$\lambda = \frac{h}{p} \quad \text{Here } h = \text{Planck's constant}$$

$p = \text{momentum of electron}$

$$\therefore \text{Momentum } (p) = \text{Mass } (m) \times \text{Velocity } (v)$$

The above relation can be derived for a photon as follows by using Einstein's equation, Planck's quantum theory and wave theory of light.



de Broglie'
(1892-1987)

A French physicist, studied history as an undergraduate in the early 1910s. His interest turned to science as a result of his assignment to radio communications in world war 1. He was awarded the Nobel Prize in physics in 1929.

$$E = mc^2 \text{ (Einstein's equation)} \quad \text{.....(i)}$$

Where E is energy, m is mass of a body and c is its velocity.

$$E = h\nu = h \times \frac{c}{\lambda} \text{ (Planck's equation)} \quad \left(\nu = \frac{c}{\lambda} \right) \quad \text{.....(ii)}$$

Combining (i) and (ii)

$$E = mc^2 = h \times \frac{c}{\lambda} \quad \text{or} \quad mc = \frac{h}{\lambda} \quad \text{or} \quad \lambda = \frac{h}{mc}$$

$$\boxed{\lambda = \frac{h}{mv} \quad \text{or} \quad \lambda = \frac{h}{p}}$$

It is clear from the above equation that the value of λ decreases on increasing either m or v or both. The wavelength of many fast-moving objects like an aeroplane or a cricket ball, is very low because of their high mass. Thus wave nature of macroscopic objects can be neglected but for microscopic particles like electrons, protons, atoms etc. wave nature is significant & cannot be neglected.

10.1 DERIVATION OF BOHR'S ANGULAR MOMENTUM QUANTIZATION RULE :

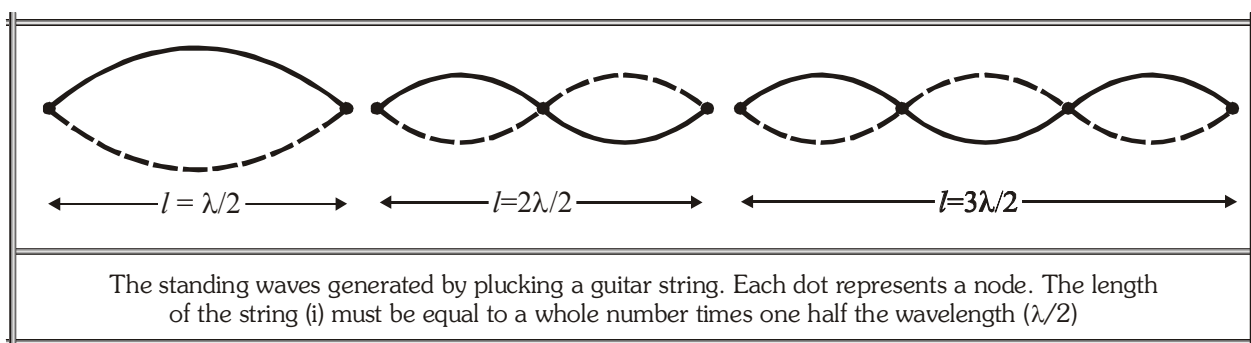
We know that according to Bohr theory, $mvr = \frac{nh}{2\pi}$

$$\text{or} \quad 2\pi r = \frac{nh}{mv} \quad (\because mv = p \text{ momentum})$$

$$\text{or} \quad 2\pi r = \frac{nh}{p} \quad \left(\because \frac{h}{p} = \lambda \text{ de-Broglie equation} \right)$$

According to de Broglie, an electron bound to the nucleus behaves like a standing wave.

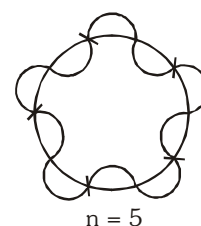
A standing wave – also known as a stationary wave – is a wave that remains in a constant position. Two opposing waves combine to form a standing wave. This phenomenon can occur because the medium is moving in the opposite direction to the wave, or it can arise in a stationary medium as a result of interference between two waves travelling in opposite directions.



For a circular standing wave to persist, a whole number of wavelength must fit into the circumference of the circle (2π).

And if n number of waves of λ wavelength are present in this circle total circumference will be $n\lambda$.

$$2\pi r = n\lambda$$



\therefore Waves made = 5

n = Number of wave made by electron in one complete revolution.

According to de Broglie

$$\lambda = \frac{h}{mv}$$

$$2\pi r = n \frac{h}{mv}$$

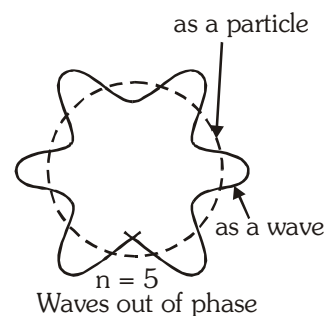
$$mvr = \frac{nh}{2\pi}$$

Therefore in $2\pi r = n\lambda$ n = Number of shell

i.e., 2nd shell $2\pi r = 2\lambda$

3rd shell $2\pi r = 3\lambda$

Electron in n^{th} orbit of any unielectron system can create 'n' waves in one complete revolution.



Ex.39 Calculate the de Broglie wavelength of a ball of mass 0.1 kg moving with a speed of 30 ms^{-1} .

Sol. $\lambda = \frac{h}{mv} = \frac{6.6 \times 10^{-34}}{0.1 \times 30} = 2.2 \times 10^{-34} \text{ m}$

This is apparent that this wavelength is too small for ordinary observation.

Although the de Broglie equation is applicable to all material objects but it has significance only in case of microscopic particles.

Ex.40 What should be the mass of the sodium photon if its wavelength is 5894 \AA , the velocity of light is $3 \times 10^8 \text{ metre/second}$ and the value of h is $6.652 \times 10^{-34} \text{ kg m}^2/\text{sec}.$

(A) 3.746×10^{-26} (B) 3.746×10^{-30} (C) 3.746×10^{-34} (D) 3.746×10^{-36}

Sol. $\lambda = \frac{h}{m \times c} \Rightarrow m = \frac{h}{c\lambda}$

$$(\because \lambda = 5894 \text{ \AA} = 5894 \times 10^{-10} \text{ m})$$

$$m = \frac{6.652 \times 10^{-34}}{3 \times 10^8 \times 5894 \times 10^{-10}} \quad \text{or} \quad \frac{6.652}{17682} \times 10^{-32}$$

$$= 0.0003746 \times 10^{-32} = 3.746 \times 10^{-36} \text{ kg}$$

Ex.41 Calculate the de-Broglie wavelength when e^- is accelerated by the following voltage.

(i) 750 V (ii) 300 volt

Sol. (i) $\lambda = \sqrt{\frac{150}{V}} \text{ \AA} = \sqrt{\frac{150}{750}} \text{ \AA} = \frac{1}{\sqrt{5}} \text{ \AA}$ (ii) $\lambda = \sqrt{\frac{150}{300}} \text{ \AA} = \frac{1}{\sqrt{2}} \text{ \AA}$

Ex.42 Find de-Broglie wavelength of electron with $KE = 9.6 \times 10^{-19} \text{ J}$.

Sol. $KE = \frac{9.6 \times 10^{-19}}{1.6 \times 10^{-19}} \text{ eV} = 6 \text{ eV}$

$$\lambda = \sqrt{\frac{150}{6}} \text{ \AA} = 5 \text{ \AA}$$

KE of 6 eV means e^- is accelerated by 6 volt.

Ex.43 Calculate the ratio of de-Broglie wavelength of electron and α -particle.

- (i) Moving at same speed
(ii) Moving at same momentum
(iii) Having same K.E.
(iv) Accelerated from rest through the same P.D.

Sol. (i) $\lambda = \frac{h}{mv}$

$$\lambda \propto \frac{1}{m}$$

$$\frac{\lambda_{\text{electron}}}{\lambda_{\alpha}} = \frac{m_{\alpha}}{m_e} = \frac{4 \times 1836}{1}$$

(ii) $\frac{\lambda_{\text{electron}}}{\lambda_{\alpha}} = \frac{1}{1}$

(iii) $\frac{h}{\sqrt{2mE}}$

$$\lambda = \frac{h}{\sqrt{2mE}} = \frac{\lambda_e}{\lambda_{\alpha}} = \sqrt{\frac{m_{\alpha}}{m_e}} = \sqrt{\frac{1836 \times 4}{1}}$$

(iv) $\lambda = \frac{h}{\sqrt{2mqV}} = \frac{\lambda_e}{\lambda_{\alpha}} = \sqrt{\frac{(mq)_{\alpha}}{(mq)_e}} = \sqrt{\frac{4 \times 2}{1/1836 \times 1}}$

Ex.44 In Li^{2+} ion electron jumps from 2^{nd} to 1^{st} orbit. If the emitted radiation is absorbed by H atom. Calculate the de-Broglie wavelength of the ejected electron.

Sol. $\Delta E = 13.6 \times 9 \left(1 - \frac{1}{4}\right) = 91.8 \text{ eV}$

Excess energy = $91.8 - 13.6 = 78.2 \text{ eV}$

$$\lambda = \sqrt{\frac{150}{78.2}} \text{ \AA} = 1.38 \text{ \AA}$$

Ex.45 Photoelectrons are liberated by ultra violet light of wavelength 2000 \AA from a metallic surface for which the photoelectric threshold is 4000 \AA . Calculate the de-Broglie wavelength of electrons emitted with maximum kinetic energy.

Solution : K.E. = Quantum Energy – Threshold energy

$$\begin{aligned} &= \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{2000 \times 10^{-10}} - \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{4000 \times 10^{-10}} \\ &= \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{10^{-10}} \left(\frac{1}{2000} - \frac{1}{4000} \right) = 4.969 \times 10^{-19} \text{ Joule.} \end{aligned}$$

$$\frac{1}{2}mv^2 = 4.969 \times 10^{-19} \Rightarrow m^2v^2 = 2 \times 4.969 \times 10^{-19} \times 9.1 \times 10^{-31}$$

$$mv = 9.51 \times 10^{-25} \Rightarrow \lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}}{9.51 \times 10^{-25}} = 0.696 \times 10^{-9} \text{ m}$$

Ex.46 Calculate the de-Broglie wavelength when proton is accelerated by the 750 V.

Sol. (i) $\lambda = \sqrt{\frac{150}{V \times 1836}} \text{ \AA} = \sqrt{\frac{150}{750 \times 1836}} \text{ \AA}$

10.2 Justification of dual nature of electrons :

I. Particle character :

- If an e^- strikes a screen coated with ZnS, it produces a spot of light called scintillation. On e^- produces only one scintillation point which means e^- are localised not spread out like wave : Photoelectric effect also proves its particle nature.
- Electron possess definite mass, momentum & KE proving their particle nature.

II. Wave character :

- It was confirmed by phenomenon of diffraction, interference, reflection.
- Davisson and Germer showed that when high speed e^- strike Ni crystal a diffraction pattern (having number of rings) is obtained like X-rays of electromagnetic spectrum.

11 HEISENBERG UNCERTAINTY PRINCIPLE :

Bohr's theory considers an electron as a material particle. Its position and momentum can be determined with accuracy. But, when an electron is considered in the form of wave as suggested by de-Broglie, it is not possible to ascertain simultaneously the exact position and velocity of the electron more precisely at a given instant since the wave is extending throughout a region of space.

In 1927, **Werner Heisenberg** presented a principle known as Heisenberg uncertainty principle which states as : **"It is impossible to measure simultaneously the exact position and exact momentum of a body as small as an electron"**.

The uncertainty of measurement of position, Δx , and the uncertainty of momentum Δp or $m\Delta v$, are related by Heisenberg's relationship as : ($p = mv$, $\Delta p = m\Delta v$)

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi} \quad \text{or} \quad \Delta x \cdot m\Delta v \geq \frac{h}{4\pi}$$

or $\Delta x \cdot \Delta v \geq \frac{h}{4\pi m}$

where h is Planck's constant.

$\Delta x \Delta v = \text{uncertainty product}$

For an electron of mass m (9.10×10^{-28} g), the product of uncertainty is quite large.

$$\Delta x \cdot \Delta v \geq \frac{6.624 \times 10^{-27}}{4\pi m} \geq \frac{6.624 \times 10^{-27}}{4 \times 3.14 \times 9.10 \times 10^{-28}}$$

$$= 0.57 \text{ erg sec per gram approximately}$$

When, $\Delta x = 0$, $\Delta v = \infty$ and vice-versa.

In the case of bigger particles (having considerable mass), the value of uncertainty product is negligible. If the position is known quite accurately, i.e., Δx is very small, Δv becomes large and vice-versa.

Ex.47 A golf ball has a mass of 40 g and a speed of 45 m/s. If the speed can be measured within accuracy of 2 %, calculate the uncertainty in the position.

Sol. Mass of the ball = 40 g = 40×10^{-3} kg

The uncertainty in the speed,

$$\Delta v = 45 \times \frac{2}{100} = 0.9 \text{ ms}^{-1}$$

$$\Delta x = \frac{h}{4\pi m \Delta v} = \frac{6.626 \times 10^{-34} \text{ Js}}{4 \times 3.14 \times (40 \times 10^{-3} \text{ kg})(0.9 \text{ ms}^{-1})} = 1.46 \times 10^{-33} \text{ m.}$$

Ex.48 Calculate the uncertainty in the velocity of a cricket ball of mass 150 g, if the uncertainty in its position is of the order of 1 Å.

($h = 6.626 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}$)

Sol. Mass of ball ,

$$m = 150 \text{ g} = 150 \times 10^{-3} \text{ kg} = 0.150 \text{ kg}$$

Uncertainty in position, $\Delta x = 1 \text{ Å} = 10^{-10} \text{ m}$

$$\Delta x \times m \Delta v = \frac{h}{4\pi}$$

$$\Delta v = \frac{h}{4\pi \times \Delta x \times m}$$

$$= \frac{6.626 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{4 \times 3.14 \times 10^{-10} \text{ m} \times 0.150 \text{ kg}}$$

$$= 3.52 \times 10^{-24} \text{ m s}^{-1}.$$

12 QUANTUM MECHANICAL MODEL OF ATOM

Classical mechanics, based on Newton's laws of motion, successfully describes the motion of all macroscopic objects such as a falling stone, orbiting planets etc., which have essentially a particle-like behaviour as shown in the previous section. However it fails when applied to microscopic objects like electrons, atoms, molecules etc. This is mainly because of the fact that classical mechanics ignores the concept of dual behaviour of matter especially for sub-atomic particles and the uncertainty principle. The branch of science that takes into account this dual behaviour of matter is called **quantum mechanics**.

Quantum mechanics is a theoretical science that deals with the study of the motions of the microscopic objects that have both observable wave like and particle like properties. It specifies the laws of motion that these objects obey. When quantum mechanics is applied to macroscopic objects (for which wave like properties are insignificant) the results are the same as those from the classical mechanics.

Quantum mechanics was developed independently in 1926 by Werner Heisenberg and Erwin Schrodinger. Here, however, we shall be discussing the quantum mechanics which is based on the ideas of wave motion. The fundamental equation of quantum mechanics was developed by Schrodinger and it won him the Nobel Prize in Physics in 1933. This equation which incorporates wave-particle duality of matter as proposed by de Broglie is quite complex and knowledge of higher mathematics is needed to solve it. You will learn its solutions for different systems in higher classes.

For a system (such as an atom or a molecule whose energy does not change with time) the Schrodinger equation is written as

$$\hat{H}\psi = E\psi$$

\hat{H} is a mathematical operator called Hamiltonian. Schrodinger gave a recipe of constructing this operator from the expression for the total energy of the system. The total energy of the system takes into account the kinetic energies of all the sub-atomic particles (electrons, nuclei), attractive potential between the electrons and nuclei and repulsive potential among the electrons and nuclei individually. Solution of this equation gives E and ψ .

12.1 Hydrogen Atom and the Schrodinger Equation

When Schrodinger equation is solved for hydrogen atom, the solution gives the possible energy levels the electron can occupy and the corresponding wave function(s) (ψ) of the electron associated with each energy level. These quantized energy states and corresponding wave functions which are characterized by a set of three quantum numbers (**principal quantum number n , azimuthal quantum number l and magnetic quantum number m_l**) arise as a natural consequence in the solution of the Schrodinger equation. When an electron is in any energy state, the wave function corresponding to that energy state contains all information about the electron.

The wave function is a mathematical function whose value depends upon the coordinates of the electron in the atom and does not carry any physical meaning. Such wave functions of hydrogen or hydrogen like species with one electron are called **atomic orbitals**.

Such wave functions pertaining to one-electron species are called one-electron systems. The probability of finding an electron at a point within an atom is proportional to the $|\psi|^2$ at that point. The quantum mechanical results of the hydrogen atom successfully predict all aspects of the hydrogen atom spectrum including some phenomena that could not be explained by the Bohr model.

Application of Schrodinger equation to multi-electron atoms presents a difficulty: the Schrodinger equation cannot be solved exactly for a multi-electron atom. This difficulty can be overcome by using approximate methods. Such calculations with the aid of modern computers show that orbitals in atoms other than hydrogen do not differ in any radical way from the hydrogen orbitals discussed above. The principal difference lies in the consequence of increased nuclear charge. Because of this all the orbitals are somewhat contracted. Further, as you shall see later, unlike orbitals of hydrogen or hydrogen like species, whose energies depend only on the quantum number n , the energies of the orbitals in multi-electron atoms depend on quantum numbers n and l .

Erwin Schrodinger, an Austrian physicist received his Ph.D. in theoretical physics from the University of Vienna in 1910. In 1927 Schrodinger succeeded Max Planck at the University of Berlin at Planck's request. In 1933, Schrodinger left Berlin because of his opposition to Hitler and Nazi policies and returned to Austria in 1936. After the invasion of Austria by Germany, Schrodinger was forcibly removed from his professorship. He then moved to Dublin, Ireland where he remained for seventeen years. Schrodinger shared the Nobel Prize for Physics with P.A.M. Dirac in 1933.



Erwin Schrodinger
(1887-1961)

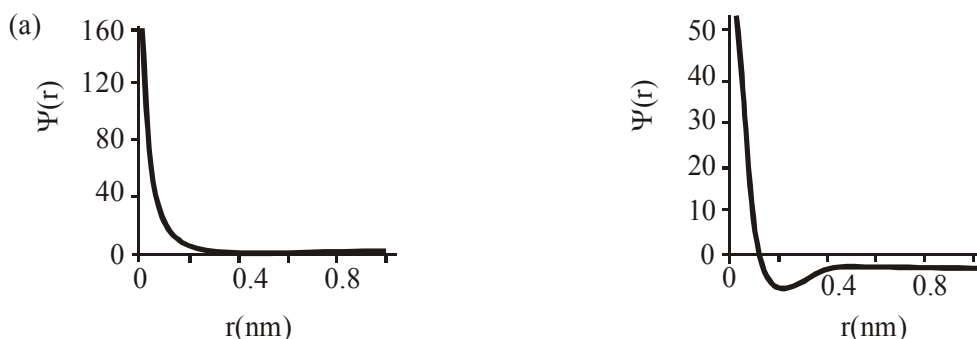
12.2 Important Features of the Quantum Mechanical Model of Atom–

Quantum mechanical model of atom is the picture of the structure of the atom, which emerges from the application of the Schrodinger equation to atoms. The following are the important features of the quantum mechanical model of atom:

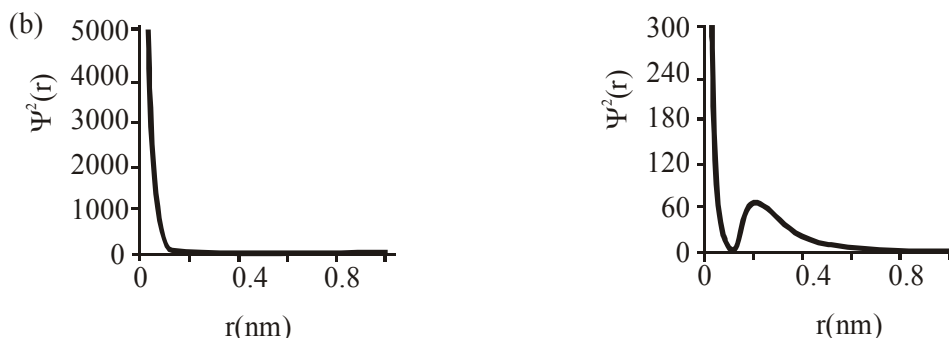
1. The energy of electrons in atoms is quantized (i.e., can only have certain specific values), for example when electrons are bound to the nucleus in atoms.
2. The existence of quantized electronic energy levels is a direct result of the wave like properties of electrons and are allowed solutions of Schrodinger wave equation.
3. Both the exact position and exact velocity of an electron in an atom cannot be determined simultaneously (Heisenberg uncertainty principle). The path of an electron in an atom therefore, can never be determined or known accurately. That is why, as you shall see later on, one talks of only probability of finding the electron at different points in an atom.
4. **An atomic orbital is the wave function ψ for an electron in an atom.** Whenever an electron is described by a wave function, we say that the electron occupies that orbital. Since many such wave functions are possible for an electron, there are many atomic orbitals in an atom. These “one electron orbital wave functions” or orbitals form the basis of the electronic structure of atoms. In each orbital, the electron has a definite energy. An orbital cannot contain more than two electrons. In a multi-electron atom, the electrons are filled in various orbitals in the order of increasing energy. For each electron of a multi-electron atom, there shall, therefore, be an orbital wave function characteristic of the orbital it occupies. All the information about the electron in an atom is stored in its orbital wave function ψ and quantum mechanics makes it possible to extract this information out of ψ .
5. The probability of finding an electron at a point within an atom is proportional to the square of the orbital wave function i.e., $|\psi|^2$ at that point. $|\psi|^2$ is known as **probability density** and is always positive. **From the value of $|\psi|^2$ at different points within an atom, it is possible to predict the region around the nucleus where electron will most probably be found.**

12.3 Shapes of Atomic Orbitals

The orbital wave function or ψ for an electron in an atom has no physical meaning. It is simply a mathematical function of the coordinates of the electron. However, for different orbitals the plots of corresponding wave functions as a function of r (the distance from the nucleus) are different. Such plots for 1s ($n = 1, l = 0$) and 2s ($n = 2, l = 0$) orbitals are

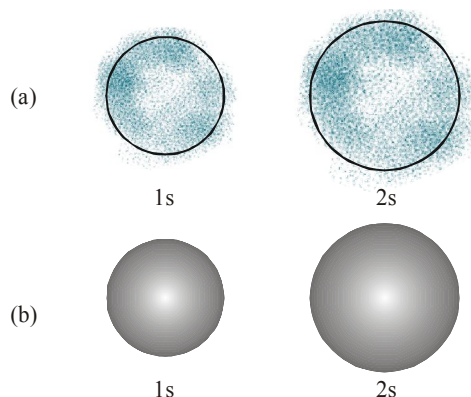


According to the German physicist, Max Born, the square of the wave function (i.e., ψ^2) at a point gives the probability density of the electron at that point. The variation of ψ^2 as a function of r for 1s and 2s orbitals is given in fig. Here again, you may note that the curves for 1s and 2s orbitals are different.



It may be noted that for 1s orbital the probability density is maximum at the nucleus and it decreases sharply as we move away from it. On the other hand, for 2s orbital the probability density first decreases sharply to zero and again starts increasing. After reaching a small maxima it decreases again and approaches zero as the value of r increases further. The region where this probability density function reduces to zero is called **nodal surfaces** or simply **nodes**. In general, it has been found that ns -orbital has $(n - 1)$ nodes, that is, number of nodes increases with increase of principal quantum number n . In other words, number of nodes for 2s orbital is one, two for 3s and so on.

These probability density variation can be visualised in terms of charge cloud diagrams. In these diagrams, the density of the dots in a region represents electron probability density in that region.

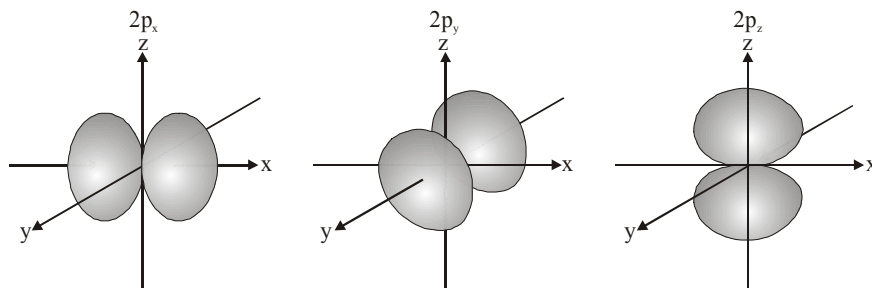


(a) Probability density plots of 1s and 2s atomic orbitals. The density of the dots represents the probability density of finding the electron in that region. (b) Boundary surface diagram for 1s and 2s orbitals.

Boundary surface diagrams of constant probability density for different orbitals give a fairly good representation of the shapes of the orbitals. In this representation, a boundary surface or contour surface is drawn in space for an orbital on which the value of probability density $|\psi|^2$ is constant. In principle many such boundary surfaces may be possible. However, for a given orbital, only that boundary surface diagram of constant probability density is taken to be good representation of the shape of the orbital which encloses a region or volume in which the probability of finding the electron is very high, say, 90%. The boundary surface diagram for 1s and 2s orbitals are given in fig. One may ask a question : Why do we not draw a boundary surface diagram, which bounds a region in which the probability of finding the electron is, 100 %? The answer to this question is that the probability density $|\psi|^2$ has always some value, howsoever small it may be, at any finite distance from the nucleus. It is therefore, not possible to draw a boundary surface diagram of a rigid size in which the probability of finding the electron is 100%. Boundary surface diagram for a s orbital is actually a sphere centred on the nucleus. In two dimensions, this sphere looks like a circle. It encloses a region in which probability of finding the electron is about 90%.

Thus we see that 1s and 2s orbitals are spherical in shape. In reality all the s-orbitals are spherically symmetric, that is, the probability of finding the electron at a given distance is equal in all the directions. It is also observed that the size of the s orbital increases with increase in n , that is, $4s > 3s > 2s > 1s$ and the electron is located further away from the nucleus as the principal quantum number increases.

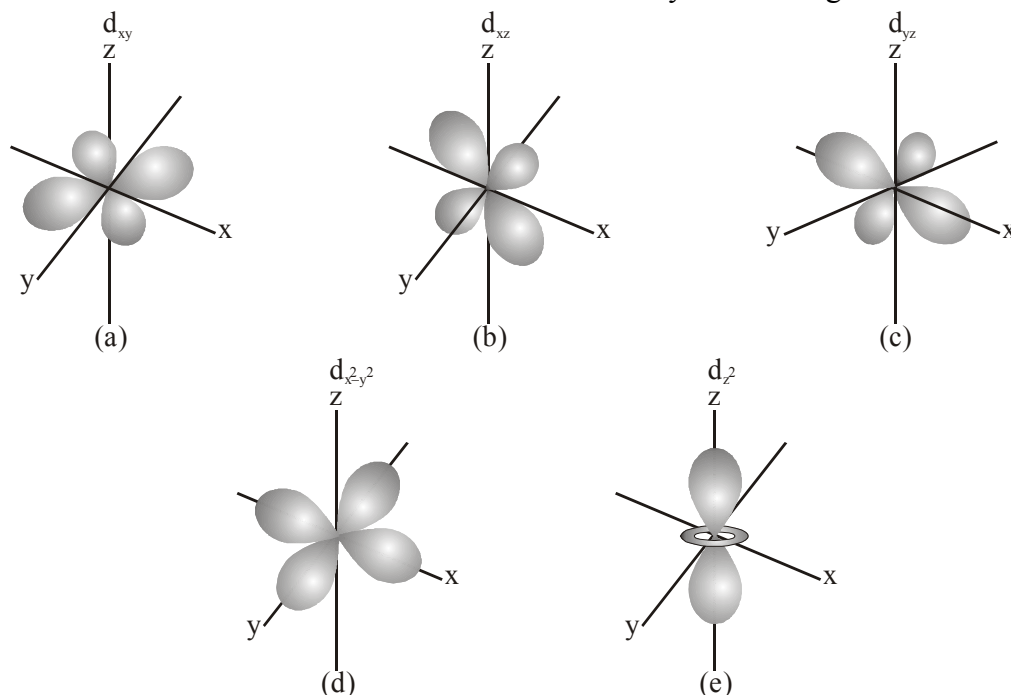
Boundary surface diagrams for three 2p orbitals ($l = 1$) are



Boundary surface diagrams of the three 2p orbitals.

In these diagrams, the nucleus is at the origin. Here, unlike s-orbitals, the boundary surface diagrams are not spherical. Instead each p orbital consists of two sections called lobes that are on either side of the plane that passes through the nucleus. The probability density function is zero on the plane where the two lobes touch each other. The size, shape and energy of the three orbitals are identical. They differ however, in the way the lobes are oriented. Since the lobes may be considered to lie along the x, y or z axis, they are given the designations $2p_x$, $2p_y$, and $2p_z$. It should be understood, however, that there is no simple relation between the values of m_l ($-1, 0$ and $+1$) and the x, y and z directions. For our purpose, it is sufficient to remember that, because there are three possible values of m_l , there are, therefore, three p orbitals whose axes are mutually perpendicular. Like s orbitals, p orbitals increase in size and energy with increase in the principal quantum number and hence the order of the energy and size of various p orbitals is $4p > 3p > 2p$. Further, like s orbitals, the probability density functions for p-orbital also pass through value zero, besides at zero and infinite distance, as the distance from the nucleus increases. The number of nodes are given by the $n - 2$, that is number of radial node is 1 for 3p orbital, two for 4p orbital and so on.

For $l = 2$, the orbital is known as d-orbital and the minimum value of principal quantum number (n) has to be 3, as the value of l cannot be greater than $n - 1$. There are five m_l values $-2, -1, 0, +1$ and $+2$ for $l = 2$ and thus there are five d orbitals. The boundary surface diagram of d orbitals are



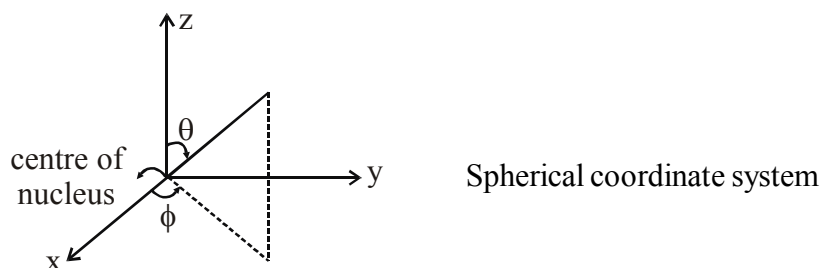
Boundary surface diagrams of the five 3d orbitals.

The five d-orbitals are designated as d_{xy} , d_{yz} , d_{xz} , $d_{x^2-y^2}$ and d_{z^2} . The shapes of the first four d-orbitals are similar to each other, whereas that of the fifth one, d_{z^2} , is different from others, but all five 3d orbitals are equivalent in energy. The d orbitals for which n is greater than 3 (4d, 5d...) also have shapes similar to 3d orbital, but differ in energy and size.

Besides the radial nodes (i.e., probability density function is zero), the probability density functions for the np and nd orbitals are zero at the plane(s), passing through the nucleus (origin). For example, in case of p_z orbital, xy-plane is a nodal plane, in case of d_{xy} orbital, there are two nodal planes passing through the origin and bisecting the xy plane containing z-axis. These are called **angular nodes** and number of angular nodes are given by ' l ', i.e., one angular node for p orbitals, two angular nodes for 'd' orbitals and so on.

The total number of nodes are given by $(n-1)$, i.e., sum of l angular nodes and $(n - l - 1)$ radial nodes.

12.4 SOLUTION OF SCHRODINGER EQUATION :



The solution in spherical coordinates may be represented as :

$$\psi = R(r) \cdot \Theta(\theta) \cdot \Phi(\phi)$$

$R(r)$: Radial function depends on n and l

$\Theta(\theta) \cdot \Phi(\phi)$: Angular function depends on l and m .

12.4.1 Radical part of solution :

$$1s \quad (n = 1, \ell = 0) : \quad R_{1s}(r) = 2 \cdot \left(\frac{Z}{a_0} \right)^{3/2} \cdot e^{-\sigma/2}$$

$$\text{where } \sigma = \frac{2Zr}{na_0} \quad a_0 = 1^{\text{st}} \text{ Bohr's radius} = 0.529 \text{ \AA}$$

$$2s \quad (n = 2, \ell = 0) : \quad R_{2s}(r) = \frac{1}{2\sqrt{2}} \cdot \left(\frac{Z}{a_0} \right)^{3/2} \cdot (2 - \sigma) e^{-\sigma/2}$$

$$2p \quad (n = 2, \ell = 1) : \quad R_{2p}(r) = \frac{1}{2\sqrt{6}} \cdot \left(\frac{Z}{a_0} \right)^{3/2} \cdot \sigma \cdot e^{-\sigma/2}$$

$$3s \quad (n=3, \ell=0): \quad R_{3s}(r) = \frac{1}{9\sqrt{3}} \cdot \left(\frac{Z}{a_0}\right)^{3/2} \cdot (6 - 6\sigma + \sigma^2)e^{-\sigma/2}$$

$$3p \quad (n=3, \ell=1): \quad R_{3p}(r) = \frac{1}{9\sqrt{6}} \cdot \left(\frac{Z}{a_0}\right)^{3/2} \cdot \sigma(4 - \sigma)e^{-\sigma/2}$$

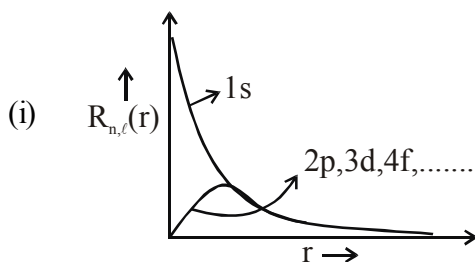
$$3d \quad (n=3, \ell=2): \quad R_{3d}(r) = \frac{1}{9\sqrt{30}} \cdot \left(\frac{Z}{a_0}\right)^{3/2} \cdot \sigma^2 \cdot e^{-\sigma/2}$$

General form :

$$R_{n\ell}(r) = K \cdot e^{-\sigma/2} \cdot \sigma^\ell \text{ (Polynomial of order } n - \ell - 1 \text{)}$$

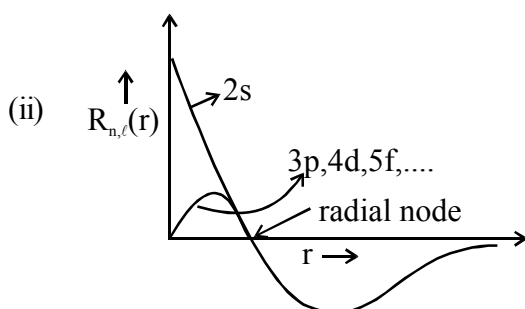
12.4.2 Graph of radial function $[R(r) \text{ or } \Psi(r)] :$

Only the graph of s-orbital does not start from origin.



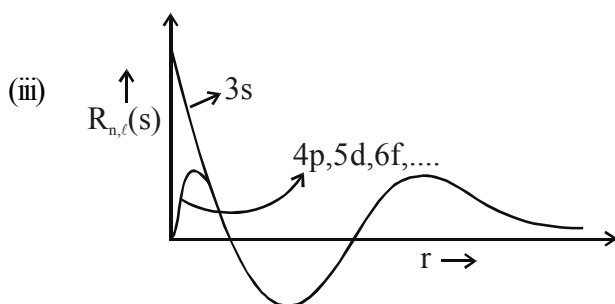
$$n - \ell - 1 = 0$$

$1s, 2p, 3d, 4f \dots$ orbitals



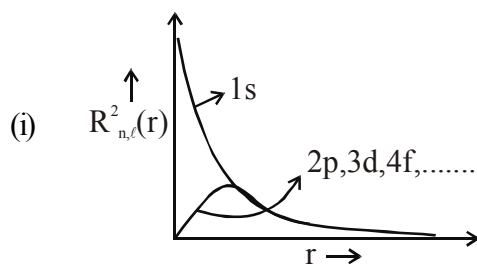
$$n - \ell - 1 = 1$$

$2s, 3p, 4d, 5f \dots$ orbitals

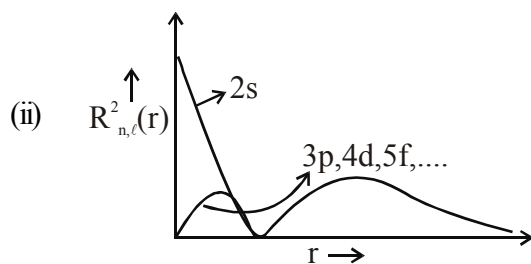


$$n - \ell - 1 = 2$$

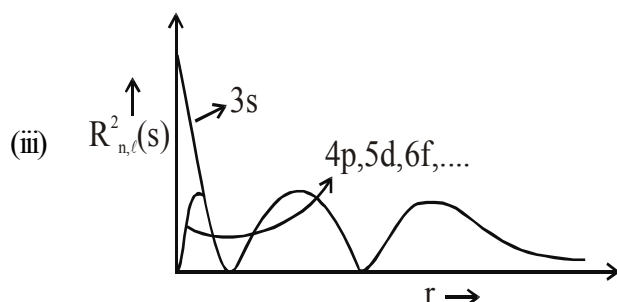
$3s, 5p, 5d, 6f \dots$ orbitals

12.4.3 GRAPH OF RADIAL PROBABILITY DENSITY FUNCTION [$R^2(r)$ or $\psi^2(r)$] :

$$n - \ell - 1 = 0, \quad (1s, 2p, 3d, 4f \dots \text{orbitals})$$



$$n - \ell - 1 = 1 \quad (2s, 3p, 4d, 5f \dots \text{orbitals})$$



$$n - \ell - 1 = 2 \quad (3s, 5p, 5d, 6f \dots \text{orbitals})$$

12.4.3 RADIAL PROBABILITY DISTRIBUTION FUNCTION (RPDF), $4\pi r^2 \psi^2(r)$

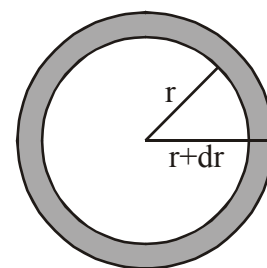
It is often useful to know the likelihood of finding the electron in an orbital at any given distance away from the nucleus. This enables us to say at what distance from the nucleus the electron is most likely to be found, and also how tightly or loosely the electron is bound in a particular atom. This is expressed by the radial probability distribution function, $4\pi r^2 \psi^2(r)$.

Radial distribution function is the measure of the probability of finding the electron in a spherical shell between thickness r and $(r + dr)$ from the nucleus, irrespective of the direction.

❖ Volume of radial shell :

$$\begin{aligned} dV &= \left[\text{Volume of sphere with radius } (r + dr) \right] - \left[\text{Volume of sphere with radius } r \right] \\ &= \frac{4}{3} \pi (r + dr)^3 - \frac{4}{3} \pi r^3 \\ &= \frac{4}{3} \pi (r^3 + 3r^2 dr + 3r dr^2 + dr^3) - \frac{4}{3} \pi r^3 = \frac{4}{3} \pi [r^3 + 3r^2 dr - r^3] \end{aligned}$$

(As dr represents an extremely small thickness, the higher powers of dr such as dr^2 and dr^3 may be neglected.)



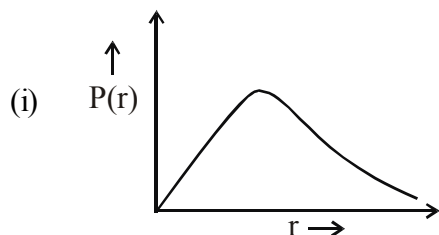
$$\therefore \text{Volume of shell, } dV = \frac{4}{3}(\pi \times 3r^2 dr) = 4\pi r^2 dr$$

$$\text{Now, radial probability density, } R^2(r) = \frac{P}{dV}$$

\therefore Probability of finding electron in the volume element,

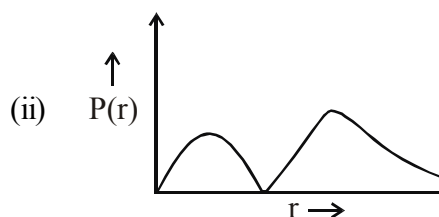
$$P = R^2(r) \cdot dV = R^2(r) \cdot 4\pi r^2 \cdot dr$$

$$\text{Now radial probability distribution function, } P(r) = \frac{P}{dr} = 4\pi r^2 \cdot R^2(r)$$



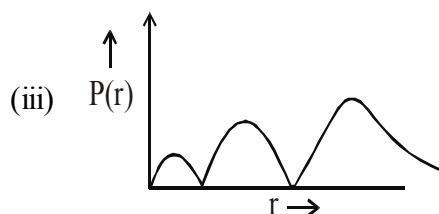
$$n - \ell - 1 = 0$$

1s, 2p, 3d, 4f orbitals



$$n - \ell - 1 = 1$$

2s, 3p, 4d, 5f orbitals



$$n - \ell - 1 = 2$$

3s, 5p, 5d, 6f orbitals

❖ Characteristics of radial distribution function :

- (i) The number of maxima in radial distribution function plot are $(n - \ell)$.
- (ii) The maximum probability of finding the electron, for the ground state hydrogen atom (1s) is found to be at a_0 (first Bohr radius).
- (iii) For 2s, 3s, 3p orbitals, the number of maxima is more than one, indicating that there is maximum probability of finding the electron at the distance corresponding to the highest value of peak.

However, there is lesser probability of finding the electron at the other peaks. It shows that in a certain state, the electron spends some portion of its time very close to the nucleus.

12.5 ANGULAR PART OF SOLUTION :

(1) s-orbital :

$$\ell = 0, m = 0 \quad \Theta(\theta) \cdot \Phi(\phi) = \sqrt{\frac{1}{4\pi}}$$

As the probability of finding electron is not depending on angle (direction) then it must be same. In all direction and hence the shape of s-orbital is sphere.

(2) p-orbital :

$$p_x\text{-orbital: } \ell = 1, m = +1 \quad \Theta(\theta) \cdot \Phi(\phi) = \sqrt{\frac{3}{4\pi}} \cdot \sin \theta \cos \phi$$

$$p_y\text{-orbital: } \ell = 1, m = -1 \quad \Theta(\theta) \cdot \Phi(\phi) = \sqrt{\frac{3}{4\pi}} \cdot \sin \theta \cos \phi$$

$$p_z\text{-orbital: } \ell = 1, m = 0 \quad \Theta(\theta) \cdot \Phi(\phi) = \sqrt{\frac{3}{4\pi}} \cdot \cos \theta$$

(3) d-orbital :

$$d_{z^2}\text{-orbital: } \ell = 2, m = 0 \quad \Theta(\theta) \cdot \Phi(\phi) = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1)$$

$$d_{x^2-y^2}\text{-orbital: } \ell = 2, m = -2 \quad \Theta(\theta) \cdot \Phi(\phi) = \sqrt{\frac{15}{4\pi}} \cdot \sin^2 \theta \cos 2\phi$$

$$d_{xy}\text{-orbital: } \ell = 2, m = +2 \quad \Theta(\theta) \cdot \Phi(\phi) = \sqrt{\frac{15}{4\pi}} \cdot \sin^2 \theta \sin 2\phi$$

$$d_{xz}\text{-orbital: } \ell = 2, m = +1 \quad \Theta(\theta) \cdot \Phi(\phi) = \sqrt{\frac{15}{4\pi}} \cdot \sin \theta \cos \theta \sin 2\phi$$

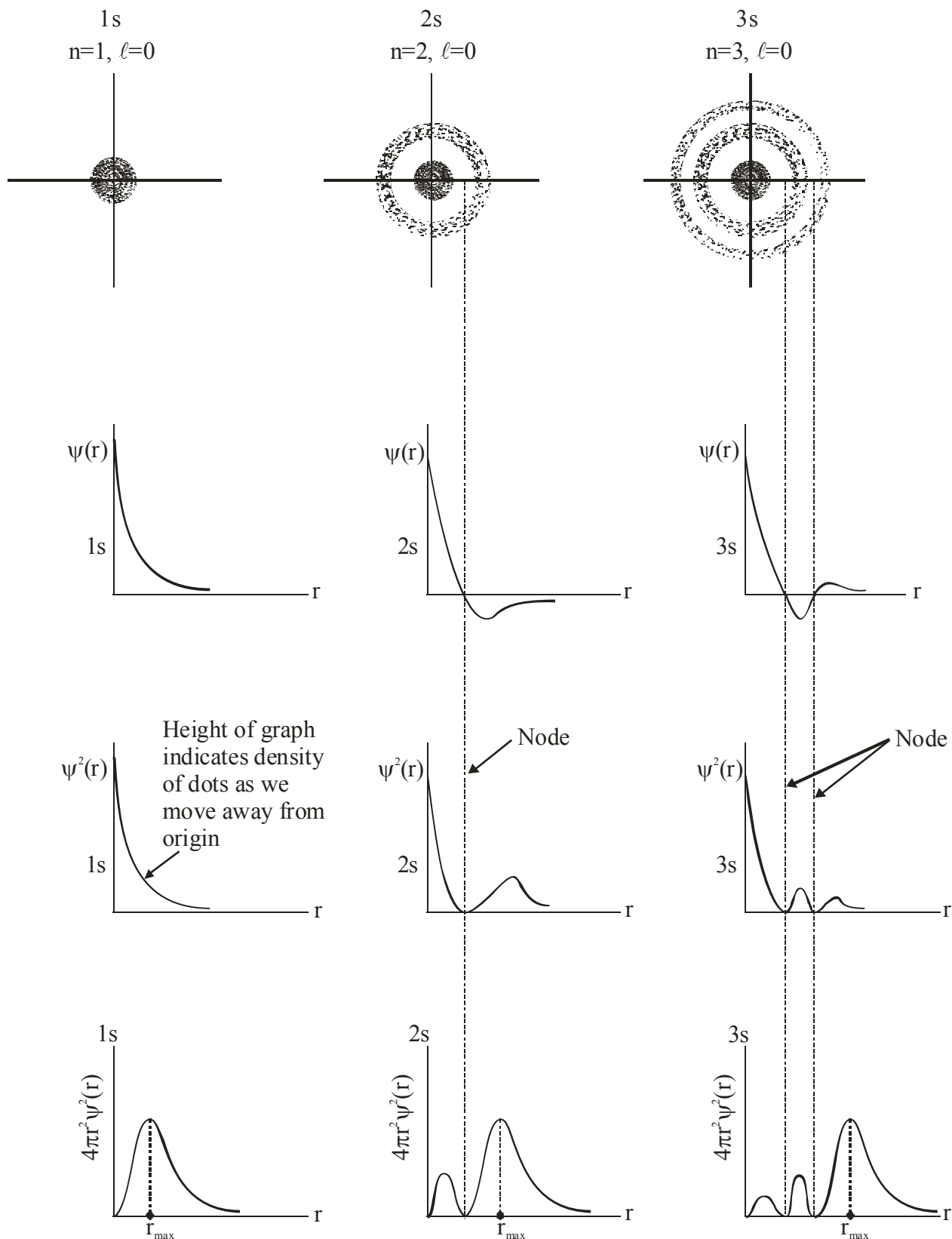
$$d_{yz}\text{-orbital: } \ell = 2, m = +1 \quad \Theta(\theta) \cdot \Phi(\phi) = \sqrt{\frac{15}{4\pi}} \cdot \sin \theta \cos \theta \cdot \sin \phi$$

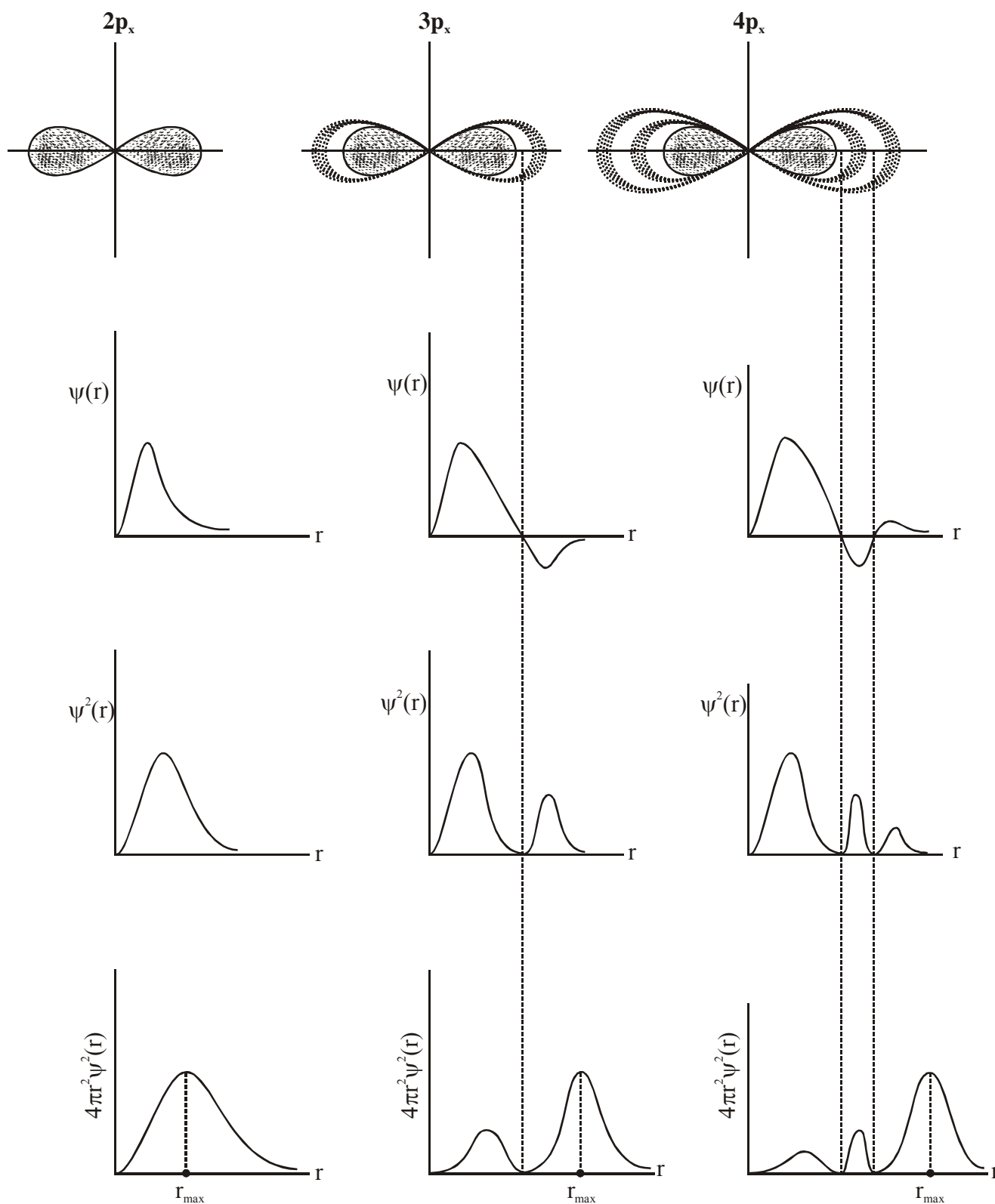
Note : Number of radial nodes = $n - \ell - 1$

Number of angular nodes = ℓ

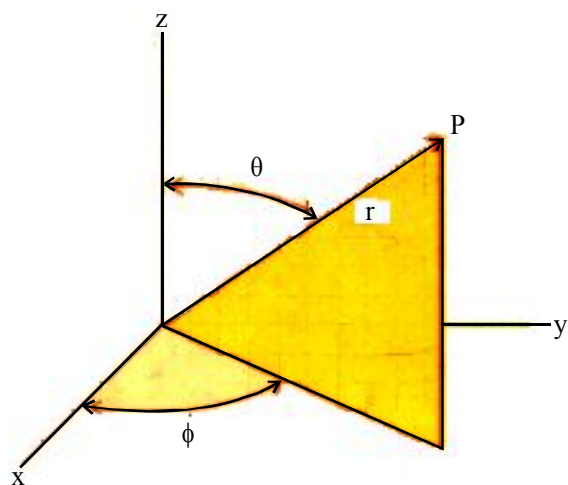
Total of number nodes = $n - 1$

12.6 Electron-density distribution in 1s, 2s and 3s-orbitals. The lower part of the fig. shows how the electron density, represented by ψ^2 varies as a function of distance from the nucleus. In the 2s and 3s - orbitals, the electron-density function drops to zero at certain distances from the nucleus. The spherical surfaces around the nucleus at which ψ^2 is zero are called nodes.

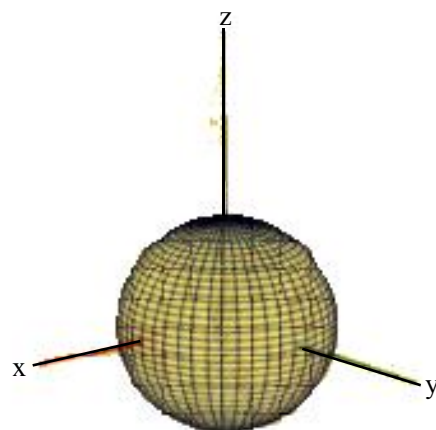


12.7 Electron-density distribution in $2p_x$, $3p_x$ and $4p_x$ -orbitals :

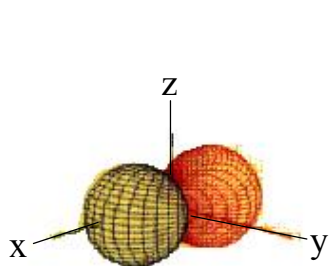
12.8 SHAPES OF ATOMIC ORBITALS



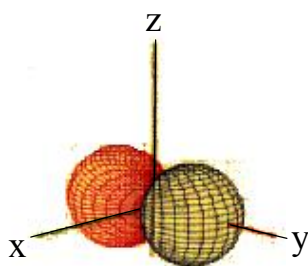
The spherical Polar Coordinates



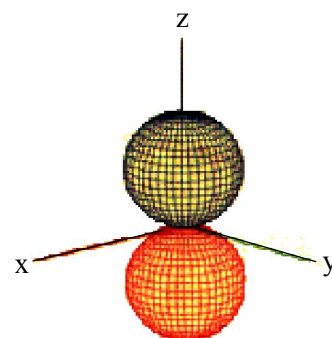
S



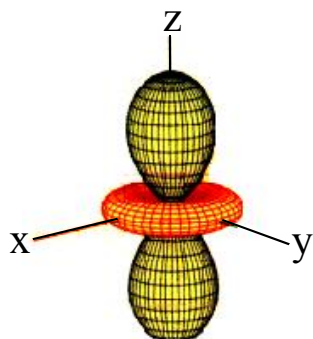
p_x



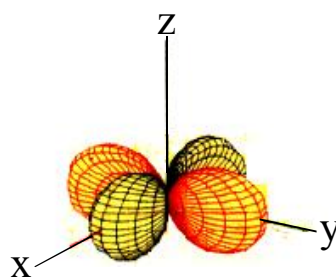
p_y



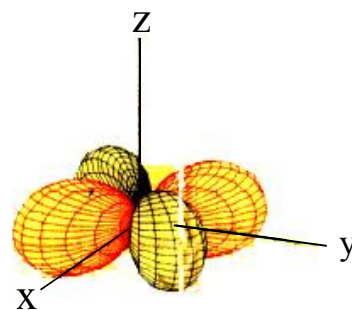
p_z



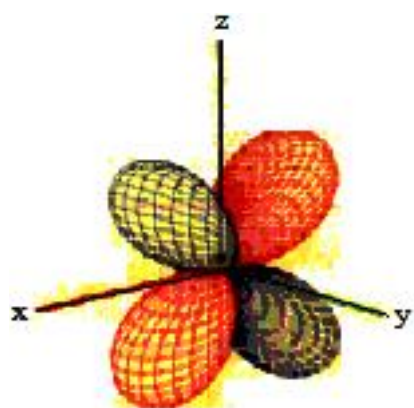
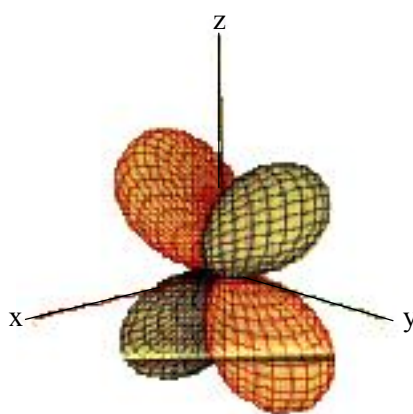
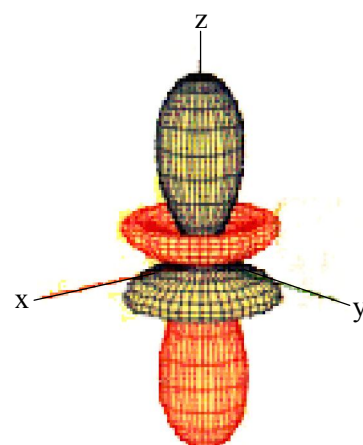
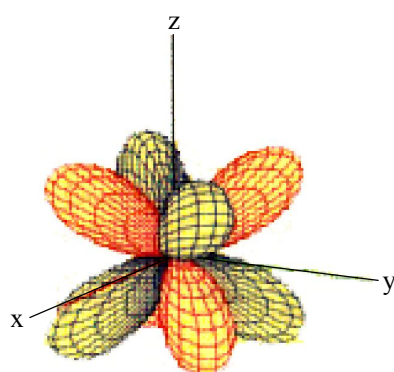
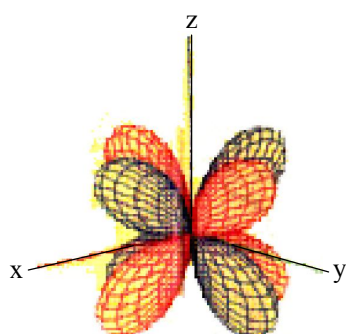
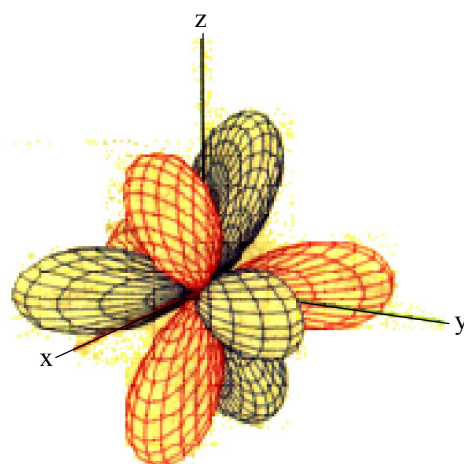
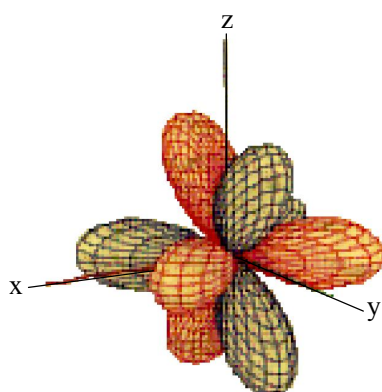
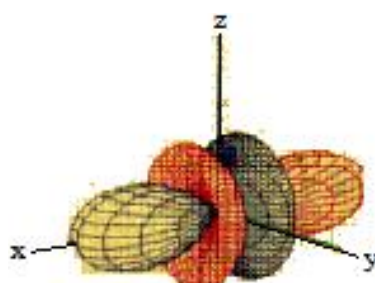
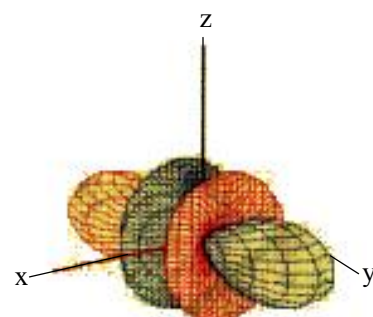
d_{z^2}



$d_{x^2-y^2}$



d_{xy}

 d_{xz}  d_{yz}  f_{z^3}  f_{xyz}  $f_{z(x^2-y^2)}$  $f_{x(y^2-z^2)}$  $f_{y(z^2-x^2)}$  f_{x^3}  f_{y^3}

Ex.49 Find the distance at which probability of finding electron is maximum for 1s orbital in a He atom.

The wave function of orbital is given as.

$$\psi_{1s} = \frac{4}{a_0^{3/2}} \cdot e^{-\frac{2r}{a_0}}$$

Sol. Probability distribution function is $P(r) = \psi^2 \cdot 4\pi r^2 = \left(\frac{16}{a_0^3}\right) e^{-\left(\frac{4r}{a_0}\right)} \cdot 4\pi r^2$

$$\Rightarrow P(r) = k \cdot r^2 \cdot e^{-\frac{4r}{a_0}}$$

$$\text{differentiating } \frac{dP(r)}{dr} = 2r \cdot e^{-\frac{4r}{a_0}} - \left(\frac{4}{a_0}\right) r^2 \cdot e^{-\frac{4r}{a_0}} = 0$$

$$\Rightarrow 1 = \frac{2r}{a_0} \Rightarrow r = \frac{a_0}{2}$$

\Rightarrow probability of finding electron is maximum at distance $\frac{a_0}{2}$ from nucleus.

Ex.50 Consider ψ (wave function) of 2s atomic orbital of H-atom is -

$$\psi_{2s} = \frac{1}{4\sqrt{2\pi} a_0^{3/2}} \left[2 - \frac{r}{a_0} \right] e^{-\frac{r}{2a_0}}$$

Find distance of radial node from nucleus in terms of a_0 .

Sol. $R(r) = 0$

$$\left[2 - \frac{r}{a_0} \right] e^{-\frac{r}{2a_0}} = 0 \Rightarrow 2 - \frac{r}{a_0} = 0 \Rightarrow r = 2 a_0$$

EXERCISE # S-I

FUNDAMENTAL PARTICLES

- Find the ratio of specific charges $\left(\frac{q}{m}\right)$ of an α -particle and a deuteron
- Specific charges of two particles A and B are in ratio 2 : 3. If their mass ratio $m_A : m_B$ is 2 : 3, then find ratio of their charges $\left(\frac{q_A}{q_B}\right)$?
- Arrange electron (e), proton (p), neutron (n) and α -particles (α), in the increasing order of their e/m ratio.
- In oil drop experiment, the following charges were experimentally determined for five oil droplets 1.2×10^{-18} unit, 3.0×10^{-18} unit, 6.0×10^{-18} unit, 2.4×10^{-18} unit and 3.6×10^{-18} unit (unit is arbitrary). What should be the charge on electron in this arbitrary unit?
- The kinetic energy of a charged particle (charge = q) accelerated by a potential difference of 10000 volt is 1.6×10^{-15} Joule. The value of 'q' is.

RUTHERFORD'S ATOMIC MODEL

- If the radius of an atom is 2\AA and the radius of its nucleus is 4×10^{-15} m. The ratio of volume of nucleus to that of atom is.
- Radius of nucleus may be given as $R_N = R_0 A^{1/3}$, where A = mass number and R_0 = constant. Calculate the density of nucleus of an atom if $R_0 = 1.2 \times 10^{-15}$.
[$N_A = 6 \times 10^{23}$, $23 \times 8\pi \times (1.2)^3 = 1000$]
- The ratio of distances of closest approach of a proton and an α -particle projected towards the same nucleus with the same initial kinetic energy is.
- An α -particle of K.E. 5.4 MeV is projected towards Cr-nucleus ($Z = 24$). What is its distance of closest approach? ($e = 1.6 \times 10^{-19}\text{C}$)
- With what speed an α -particle should be projected towards stationary krypton nucleus ($Z = 36$) such that it approaches upto $2.4 \times 10^{-14}\text{m}$ from the nucleus? ($N_A = 6 \times 10^{23}$, $e = 1.6 \times 10^{-19}\text{C}$).

WAVE CHARACTERISTICS

- Calculate the wave length of an electromagnetic radiation of frequency 2×10^{15} Hz.
- A radiostation emits the radiations of wavelength 2000 m (meter band of station). What is the frequency band of that station (Frequency of emitted radio waves)?
- The wave numbers of two electromagnetic radiations are $4 \times 10^6 \text{ m}^{-1}$ and $2 \times 10^5 \text{ cm}^{-1}$. The ratio of their frequencies is.
- An electromagnetic radiation makes 5000 waves in 20 cm. The frequency of radiation is.

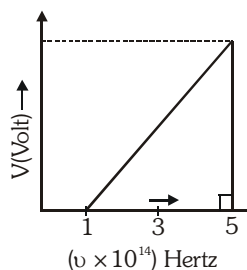
PLANCK'S QUANTUM THEORY

- Calculate the energy in Joule of a photon of wave length 4000 \AA .

16. The eyes of certain member of the reptile family pass a single visual signal to the brain when the visual receptors are struck by photons of wavelength 662 nm. If a total energy of 3.0×10^{-14} J is required to trip the signal, what is the minimum number of photons that must strike the receptor.
($h = 6.62 \times 10^{-34}$ J \times s)
17. Find the number of photons of radiation of frequency 5×10^{13} s⁻¹ that must be absorbed in order to melt one gm ice when the latent heat of fusion of ice is 330 J/g. ($h = 6.6 \times 10^{-34}$ J \times sec.)
18. A certain dye absorbs 4000 Å and fluoresces at 5000 Å these being wavelengths of maximum absorption that under given conditions 40% of the absorbed energy is emitted. Calculate the ratio of the number of quanta emitted to the number absorbed.
19. The reaction between H₂ and Br₂ to form HBr in presence of light is initiated by the photo decomposition of Br₂ into free Br atoms (free radicals) by absorption of light. The bond dissociation energy of Br₂ is 192 KJ/mole. What is the longest wavelength (in Å) of the photon that would initiate the reaction.
 $\left(1 \frac{\text{eV}}{\text{atom}} = 96 \text{ kJ/mol} ; hc = 1240 \text{ eV} \times \text{nm}\right)$
20. The quantum yield for decomposition of HI is 0.2. In an experiment 0.01 moles of HI are decomposed. Find the number of photons absorbed. ($N_A = 6 \times 10^{23}$)

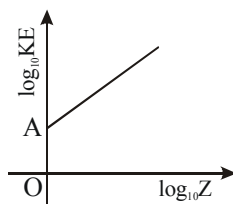
PHOTOELECTRIC EFFECT

21. The minimum energy required for the emission of a metal electron is 13.24×10^{-19} J. Calculate the critical frequency and the corresponding wavelength of the photon (threshold wavelength) required to eject the electron ?
22. A light source of wavelength λ illuminates a metal and ejects photo electron with $(KE)_{\text{max}} = 1$ eV. Another light source of wave length $\frac{\lambda}{3}$, ejects photoelectrons from same metal with $(KE)_{\text{max}} = 5$ eV. Find the value of work function (eV) of metal.
23. The dissociation energy of H₂ is 482.5 KJ/mol. If H₂ is exposed to radiant energy of wavelength 124 nm, what % of radiant energy will be converted into K.E. ($1 \frac{\text{eV}}{\text{atom}} = 96.5 \text{ kJ/mol.}$)
24. The K.E. of an electron emitted from tungsten surface is 3.06 eV. What voltage would be required to bring the electron to rest.
25. Stopping potential [V volts] is plotted against frequency of light used [ν]. Find work function (eV). ($h = 6.62 \times 10^{-34}$ J \times s)



BOHR'S MODEL

26. If the mass of electron is doubled, then find the new radius (in Å) of 1st orbit of H-atom?
27. If an electron in H-atom jumps from one orbit to other its angular momentum doubles. If the new radius is 'x' times the old radius, then find x ?
28. The radius of the an orbit of hydrogen atom is 0.85 nm. Calculate the velocity (in m/sec) of electron in this orbit.
29. The velocity of e^- in a certain Bohr orbit of the hydrogen atom bears the ratio 1:275 to the velocity of light. What is the quantum no. "n" of the orbit and the wave no. of the radiation emitted for the transition from the quatum state (n+1) to the ground state.
30. If the average life time of an excited state of H atom is of order 10^{-8} sec, estimate how many orbits an e^- makes when it is in the state $n = 2$ and before it suffers a transition to $n = 1$ state.
31. Calculate the frequency of e^- in the first Bohr orbit in a H-atom.
32. Calculate energy (in J) of electron which is moving in the orbit of a hydrogen atom that has its radius, sixteen times the radius of first Bohr orbit for H-atom.
33. The energy of an excited H-atom is -3.4 eV. Calculate angular momentum of e^- in the given orbit.
34. In a H-like atom for an electron revolving in n^{th} orbit, the variation of $\log_{10} \text{KE}$ versus $\log_{10} Z$ is plotted as following -



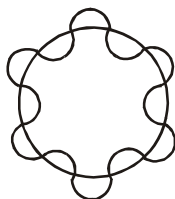
where Z is atomic number & KE is kinetic energy of electron (in eV). If $OA = \log_{10} 3.4$ then find the value of principle quantum number of the electron.

35. The energy of the second stationary state in Li^{+2} ion is -11.025×10^{-18} J. Find ionization energy (in J/mole) for He^+ ions in its ground state :
36. The energy of an electron in the first orbit of He^+ is -871.6×10^{-20} J. The energy of the electron in the first orbit of hydrogen would be :
37. A single electron orbits around a stationary nucleus of charge $+Ze$ where Z is atomic number and ' e ' is the magnitude of the electric charge. The hydrogen like species required 47.2 eV to excite the electron from the second Bohr orbit to the third Bohr orbit. Find
 - (i) the value of Z and give the hydrogen like species formed.
 - (ii) the kinetic energy (in eV) and potential energy (in eV) of the electron in the first Bohr orbit.
38. A hydrogen like atom with atomic number ' Z ' is in higher excited state of quantum number ' n '. This xcited state atom can make a transition to the first excited state by successively emitting two photons of energies 10 eV and 68.2 eV respectivley. Alternatively, the atom from the same excited state can make a transition to the 2nd excited state by emitting two photons of energies 4.25 eV and 5.95 eV respectively. Calculate the value of ' Z '.

39. H-atom is exposed to electromagnetic radiation of 1026 \AA and gives out induced radiations (radiations emitted when e^- returns to ground state). Calculate λ (in \AA) of induced radiations.
40. Estimate the difference in energy (in eV) between I and II Bohr Orbit for a hydrogen atom. At what minimum atomic number a transition from $n=2$ to $n=1$ energy level would result in the emission of X-rays with $\lambda = 3.0 \times 10^{-8} \text{ m}$? Which hydrogen like species does this atomic number correspond to.
41. A doubly ionised lithium atom is hydrogen like with atomic number $z = 3$. Find the wavelength (in \AA) of the radiation required to excite the electron in Li^{2+} from the first to the third Bohr orbit.
42. If shortest wavelength of H-atom in Balmer series is X then.
 - (i) What is the shortest wave length in Lyman series.
 - (ii) What is the longest wave length in Paschen series.
43. Ionization energy of H-atom is 13.6 eV . If H-atoms in the ground state are excited by monochromatic light of energy 12.1 eV then the maximum number of spectral lines emitted according to Bohr's theory will be -
44. Find the number of spectral lines in Paschen series emitted by atomic H, when electron is excited from ground state to 7^{th} energy level returns back.
45. A stationary He^+ ion emitted a photon corresponding to a first line of the Lyman series. The photon liberated a photoelectron from a stationary H atom in ground state. What is the velocity (in cm/sec.) of photoelectron.

DE-BROGLIE AND HEISENBERG EQUATION

46. The figure shows a sample of H-atoms having electron revolving in higher orbit 'n'.



If this electron makes transition from this orbit 'n' to ground state, No. of paschen lines emtted are.

47. deBroglie wavelength associated with an electron in 4^{th} orbit of hydrogen atom is $a \times (\pi r_0)$ where r_0 is radius of 1^{st} orbit of hydrogen atom, find value of 'a'.
48. The minimum number of waves made by a Bohr electron in an orbit of maximum magnetic quantum number 3 will be -
49. Calculate the de-broglie wavelength (in m) associated with motion of earth (mass $6 \times 10^{24} \text{ Kg}$) orbiting around the sun at a speed of $3 \times 10^6 \text{ m/s}$.
50. What is de Broglie wavelength (in pm) associated with an e^- accelerated through potential difference = 15 KV .
51. To what effective potential (in volt) a proton beam be subjected to give its protons a wavelength of $1 \times 10^{-10} \text{ m}$.
52. A proton is accelerated to one- tenth of the velocity of light. If its velocity can be measured with a precision ± 1 . What must be its uncertainty in position (in m). (Use : $\frac{h}{4\pi} = 5.2 \times 10^{-35}$)

53. The uncertainty in the position of an electron (mass 9.1×10^{-28} gm) moving with a velocity of 3×10^4 cm sec $^{-1}$, uncertainty in velocity is 0.011% will be : ($h = 6.6 \times 10^{-34}$ J \times s)
54. If uncertainties in measurement of position and momentum of an electron are equal, then the uncertainty in measurement of its velocity is $x \times 10^{12}$. The value of x (the closest whole number value) is
 $m_e = 9.1 \times 10^{-31}$ kg, and $h = 6.625 \times 10^{-34}$ Js.
55. With the help of Heisenberg's uncertainty principle, show that electron can never exist in the nucleus.

SCHRODINGER EQUATION

56. Calculate the distance of spherical nodes for '3s' orbital from nucleus?

$$R_{3s} = \frac{1}{9\sqrt{3}a_0^{3/2}} (6 - 6\sigma + \sigma^2) e^{-\frac{\sigma}{2}} \quad \text{where } \sigma = \frac{2r}{na_0}$$

57. How many non-spherical subshell are possible that have atleast two maxima if a curve is plotted between radial probability distribution function versus radial distance for which principal quantum number: $n \leq 4$?
58. The ratio of angular nodes of 3d orbital and radial nodes of 3p orbital is $x : 1$ what is the value of x .
59. For an orbital in B^{+4} radial function is :

$$R(r) = \frac{1}{9\sqrt{6}} \left(\frac{Z}{a_0} \right)^{\frac{3}{4}} (4 - \sigma) \sigma e^{-\sigma/2}$$

where $\sigma = \frac{Zr}{a_0}$ and $a_0 = 0.529 \text{ \AA}$; Z = atomic number, r = radial distance from nucleus.

The radial node of orbital is at distance from nucleus.

60. Total nodes in 5f-orbital is.

EXERCISE # S-II

- ' α particle' of 3.6 MeV are fired towards nucleus A_ZX , at point of closest separation distance between ' α particle' and 'X' is 1.6×10^{-14} m. Calculate atomic number of 'X'
[Given : $1/4\pi\epsilon_0 = 9 \times 10^9$ in S.I. units]
- Suppose the potential energy between electron and proton at a distance r is given by $-\frac{ke^2}{3r^3}$. Use Bohr's theory to obtain energy of such a hypothetical atom.
- In the Bohr's model, for unielectronic species following symbols are used
 $r_{n,z}$ \longrightarrow Radius of n^{th} orbit with atomic number "z"
 $U_{n,z}$ \longrightarrow Potential energy of electron in n^{th} orbit with atomic number "z"
 $K_{n,z}$ \longrightarrow Kinetic energy of electron in n^{th} orbit with atomic number "z"
 $v_{n,z}$ \longrightarrow Velocity of electron in n^{th} orbit with atomic number "z"
 $T_{n,z}$ \longrightarrow Time period of revolution of electron in n^{th} orbit with atomic number "z"
 Calculate z in all in cases.
 (i) $U_{1,2} : K_{1,z} = -8 : 1$ (ii) $r_{1,z} : r_{2,1} = 1 : 8$
 (iii) $v_{1,z} : v_{3,1} = 9 : 1$ (iv) $T_{1,2} : T_{2,z} = 9 : 32$
- In a hypothetical H-atom the mass of electron & its charge is double of what we consider then calculate the total energy (in eV) of electron in the Ist orbit of such a hypothetical H-atom ?
[Assuming all others concepts and parameter to be same as we considered in Bohr's model.]
- In H-spectrum, longest wavelength of Lyman is 120 nm and shortest wavelength of Balmer is 360 nm. From this data, find longest wavelength of photon, that can ionize this H-atom
- A proton and an electron, both at rest initially, combine to form a H-atom in ground state. A single photon is emitted in this process. Find the wavelength (in nm) of this photon
(use : $hc = 1237.6 \text{ eV} \times \text{nm}$)
- A H-like ion is observed to emit six different wavelengths originating from all possible transitions between a group of levels. These levels have energies between -0.85 eV (Min) and -0.544 eV (Max).
 (a) Find atomic number (z) of element
 (b) Find quantum numbers of levels between which transitions occur.
 (c) Calculate largest wavelength emitted in transits between the levels.
- The angular momentum of an electron in a Bohr's orbit of H-atom is $3.1652 \times 10^{-34} \text{ kg-m}^2/\text{sec}$. Calculate the wavenumber in terms of Rydberg constant (R) of the spectral line emitted when an electron falls from this level to the ground state. [Use $h = 6.626 \times 10^{-34} \text{ Js}$]
- The ionisation energy of the hydrogen atom is given to be 13.6 eV. A photon falls on a hydrogen atom which is initially in the ground state and excites it to the ($n = 4$)state.
 (a) show this transition in the energy-level diagram &
 (b) calculate the wavelength (in Å) of the photon.

10. The ionisation energy of a H-like Bohr atom is 4 Rydbergs
- (i) What is the wavelength (in Å) of radiation emitted when the e^- jumps from the first excited state to the ground state.
- (ii) What is the radius (in cm) of first Bohr orbit for this atom. [**1 Rydberg = 2.18×10^{-18} J**]
11. Photon having wavelength 12.4 nm was allowed to strike a metal plate having work function 25 eV. Calculate the
- (a) Maximum kinetic energy (in eV) of photoelectrons emitted in eV.
- (b) Wavelength (in Å) of electron with maximum kinetic energy in Å.
- (c) Calculate the uncertainty in wavelength (in m) of emitted electron if the uncertainty in the momentum is 6.62×10^{-28} Kg m/sec.
-
12. The diameter of a dust particle of mass 10^{-3} gm is 2 Å . If uncertainty in speed of this particle is $\frac{3.31}{\pi} \times 10^{-3}$ m/s, then find minimum uncertainty in its position
13. The vapours of Hg absorb some electrons accelerated by a potential diff. of 4.5 volt as a result of which light is emitted. If the full energy of single incident e^- is supposed to be converted into light emitted by single Hg atom, find the wave no. (in m^{-1}) of the light.
14. A photon having $\lambda = 960\text{ Å}$ causes the ionization of a nitrogen atom. Give the I.E. per mole of nitrogen in KJ.
- (Use : $hc = 1240\text{ eV} \times \text{nm}$ and $1 \frac{\text{eV}}{\text{atom}} = 96.0\text{ kJ/mol}$.)
15. Mr. Santa has to decode a number "ABCDEF" where each alphabet is represented by a single digit. Suppose an orbital whose radial wave function is represented as

$$\Psi_{(r)} = k_1 \cdot e^{-r/k_2} (r^2 - 5k_3r + 6k_3^2)$$

From the following information given about each alphabet then write down the answers in the form of "ABCDEF", for above orbital.

Info A = Value of n where " n " is principal quantum number

Info B = No. of angular nodes

Info C = Azimuthal quantum number of subshell to orbital belongs

Info D = No. of subshells having energy between $(n+5)s$ to $(n+5)p$ where n is principal quantum number

Info E = Orbital angular momentum of given orbital.

Info F = Radial distance of the spherical node which is farthest from the nucleus

(Assuming $k_3 = 1$)

EXERCISE # O-I

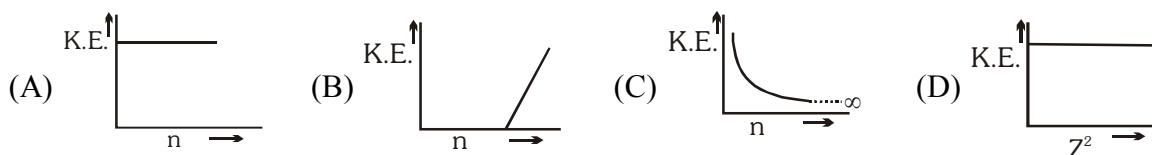
1. Anode rays are made up of :
(A) only protons (B) only nucleus of atom
(C) Positive residue of atoms (D) only electrons
2. When Lithium (${}^7_3\text{Li}$) vapours were filled in discharge tube for anode ray experiment, the anode rays were found to contain only Li^+ ions. Thus the anode ray particle contains :
(A) 1 proton only (B) 3 proton and 4 neutron only
(C) 3 proton, 4 neutron and 2 electrons (D) 3 proton, 3 neutrons and 3 electrons
3. The specific charge is maximum for
(A) Na^+ (B) Al^{+3} (C) H^+ (D) Mg^{+2}
4. Which of the following particle is not deflected in the magnetic field
(A) Electron (B) proton (C) Neutron (D) Deuteron
5. E/m ratio of a particle of charge 2 unit and mass 4 amu is
(A) $4.8 \times 10^7 \text{ C/kg}$ (B) 0.5 C/kg (C) $4.8 \times 10^4 \text{ C/kg}$ (D) $8 \times 10^{-20} \text{ C/kg}$
6. α -particles are projected towards the nucleus of following metals, with the same kinetic energy. The distance of closest approach will be minimum for which metal?
(A) Cu (B) Ag (C) Au (D) Ca
7. Which of the following is not a conclusion of Rutherford's atomic model -
(A) Most of the part inside an atom is empty
(B) Almost all mass of an atom is concentrated in the nucleus.
(C) The size of nucleus is very small in comparison to the size of atom
(D) Electron revolves around the nucleus in definite orbits.
8. In the different experiments, α -particles, proton, deuteron and neutron are projected towards gold nucleus with the same kinetic energy. The distance of closest approach will be minimum for
(A) α -particle (B) proton (C) dueteron (D) neutron
9. The ratio of the energy of a photon of 2000 \AA wavelength radiation to that of 4000 \AA radiation is
(A) $1/4$ (B) 4 (C) $1/2$ (D) 2
10. Small packets of light is called
(A) proton (B) quanta (C) photon (D) spectrum
11. Which of the following electromagnetic radiation have greater frequency?
(A) X - rays (B) Ultraviolet rays (C) Radio waves (D) Visible rays
12. Two electromagnetic radiations have wave numbers in the ratio $2 : 3$. Their energies per quanta will be in the ratio
(A) $3 : 2$ (B) $9 : 4$ (C) $4 : 9$ (D) $2 : 3$

13. A radio station is emitting the radiations of frequency 2×10^4 Hz. If its frequency is doubled,
 (A) wavelength will be doubled (B) energy per quanta will be doubled
 (C) wave number will be halved (D) all of these
14. A photon of 400 nm is absorbed by a gas molecule and then the molecule re-emits two photons. One re-emitted photon has wavelength 500 nm. Assuming that there is no change in the energy of molecule, the wavelength of second re-emitted photon is
 (A) 100 nm (B) 2000 nm (C) -100 nm (D) 900 nm
15. A green bulb and a red bulb are emitting the radiations with equal power. The correct relation between numbers of photons emitted by the bulbs per second is
 (A) $n_g = n_r$ (B) $n_g < n_r$ (C) $n_g > n_r$ (D) unpredictable
16. The threshold wavelength for ejection of electrons from a metal is 330 nm. The work function for the photoelectric emission from the metal is ($h = 6.6 \times 10^{-34}$ J-s)
 (A) 1.2×10^{-18} J (B) 6.0×10^{-19} J (C) 1.2×10^{-20} J (D) 6.0×10^{-12} J
17. In the emission of photoelectrons, the number of photoelectrons emitted per unit time depends upon
 (A) energy of the incident radiation (B) intensity of the incident radiation
 (C) frequency of the incident radiation (D) wavelength of the incident radiation
18. Radiations of frequency, ν , are incident on a photosensitive metal. The maximum kinetic energy of photoelectrons is 'E'. When the frequency of the incident radiations is doubled, what is the maximum kinetic energy of the photoelectrons?
 (A) 2E (B) E/2 (C) $E + h\nu$ (D) $E - h\nu$
19. Radiation of $\lambda = 155$ nm was irradiated on Li (work function = 5 eV) plate. The stopping potential (in V) is _____.
 (A) 3 V (B) 8 V (C) 9 V (D) 5 V
20. Electromagnetic radiations having $\lambda = 310$ Å are subjected to a metal sheet having work function = 12.8 eV. What will be the velocity of photoelectrons with maximum Kinetic Energy..
 (A) 0, no emission will occur (B) 2.18×10^6 m/s
 (C) $2.18\sqrt{2} \times 10^6$ m/s (D) 8.72×10^6 m/s
21. Bohr's model may be applied to
 (A) Na^{10+} ion (B) He atom (C) Be^{2+} ion (D) C^{6+} ion
22. If the radius of 3rd Bohr's orbit of H is x, then radius of 4th orbit of Li^{2+} ion would be :-
 (A) $\frac{27}{16}x$ (B) $\frac{16}{27}x$ (C) $\frac{9}{16}$ (D) None of these
23. What would be the approximate quantum number, n, for a circular orbit of hydrogen, 1×10^{-5} cm in diameter?
 (A) 31 (B) 43 (C) 40 (D) 39

24. If the mass of electron is doubled, the radius of first orbit of H-atom become about
(A) 0.529 \AA (B) 0.265 \AA (C) 1.058 \AA (D) 0.32 \AA
25. The speed of electron revolving in the 4th orbit of a hydrogen like atom or ion is 1094 km/s . The atom or ion is
(A) H (B) He^+ (C) Li^{2+} (D) Be^{3+}
26. How much distance an electron revolving in 3rd orbit of He^+ ion will travel in one second
(A) $1.458 \times 10^6 \text{ m}$ (B) $3.28 \times 10^6 \text{ m}$ (C) $4.862 \times 10^5 \text{ m}$ (D) $2.917 \times 10^6 \text{ m}$
27. The ratio of time taken by electron in revolutions round the H-nucleus in 2nd and 3rd orbits, are
(A) $2 : 3$ (B) $4 : 8$ (C) $8 : 27$ (D) $27 : 8$
28. Which of the following is not a permissible value of angular momentum of electron in H-atom?
(A) $1.5 \frac{h}{\pi}$ (B) $0.5 \frac{h}{\pi}$ (C) $1.25 \frac{h}{\pi}$ (D) all of these
29. Angular momentum for P-shell electron :-
(A) $\frac{3h}{\pi}$ (B) Zero (C) $\frac{\sqrt{2}h}{2\pi}$ (D) None
30. Angular momentum in 2nd Bohr orbit of H-atom is x . Then find out angular momentum in 1st excited state of Li^{+2} :-
(A) $3x$ (B) $9x$ (C) $x/2$ (D) x
31. The orbit from which when electron will jump in other orbit, energy may be absorbed but not emitted out, will be
(A) 1st orbit (B) 2nd orbit (C) 7th orbit (D) infinite orbit
32. The potential energy of electron revolving in the ground state of H-atom is
(A) -13.6 eV (B) -6.8 eV (C) -27.2 eV (D) Zero
33. If the potential energy (PE) of hydrogen electron is -3.02 eV then in which of the following excited level is electron present :-
(A) 1st (B) 2nd (C) 3rd (D) 4th
34. A single electron is revolving in orbits around a stationary nucleus ($z = 5$). The energy required to excite the electron from third to fourth Bohr orbit will be :-
(A) 4.5 eV (B) 8.53 eV (C) 25 eV (D) 16.53 eV
35. A photon of energy 12.75 eV is completely absorbed by a hydrogen atom initially in ground state. The principle quantum number of the excited state is
(A) 1 (B) 3 (C) 4 (D) ∞

36. An hydrogen atom (ionisation energy 13.6 eV) jumps from third excited state to first excited state. The energy of photon emitted in the process is
 (A) 1.89 eV (B) 2.55 eV (C) 12.09 eV (D) 12.75 eV

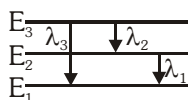
37. Which is correct graph :-



38. The energy required to remove an electron from the surface of sodium metal is 3.3 eV. What is the longest wavelength of radiation with which it can show photoelectric effect?

Use $h = 6.6 \times 10^{-34} \text{ J.s}$

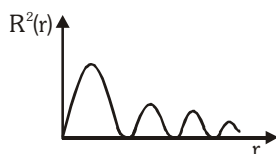
- (A) $1.75 \times 10^{-7} \text{ m}$ (B) $3.75 \times 10^{-5} \text{ m}$ (C) $1.75 \times 10^{-5} \text{ m}$ (D) $3.75 \times 10^{-7} \text{ m}$
39. Which is correct for any H like species :-
 (A) $(E_2 - E_1) > (E_3 - E_2) > (E_4 - E_3)$ (B) $(E_2 - E_1) < (E_3 - E_2) < (E_4 - E_3)$
 (C) $(E_2 - E_1) = (E_3 - E_2) = (E_4 - E_3)$ (D) $(E_2 - E_1) = 1/4 (E_3 - E_2) = 1/9 (E_4 - E_3)$
40. A single electron orbits a stationary nucleus of charge $+Ze$, where Z is a constant. It requires 47.2 eV to excite electron from second Bohr orbit to third Bohr orbit, find the value of Z :-
 (A) 1 (B) 3 (C) 5 (D) 4
41. The energy of H-atom in n^{th} orbit is E_n then energy in n^{th} orbit of singly ionised helium atom will be:
 (A) $4E_n$ (B) $E_n/4$ (C) $2E_n$ (D) $E_n/2$
42. Which electronic level would allow the hydrogen atom to absorb a photon but not to emit a photon
 (A) 3s (B) 2p (C) 2s (D) 1s
43. The third line in Balmer series corresponds to an electronic transition between which Bohr's orbits in hydrogen
 (A) $5 \rightarrow 3$ (B) $5 \rightarrow 2$ (C) $4 \rightarrow 3$ (D) $4 \rightarrow 2$
44. In the following transition which statement is correct



- (A) $E_{3-1} = E_{3-2} - E_{2-1}$ (B) $\lambda_3 = \lambda_1 + \lambda_2$
 (C) $\nu_3 = \nu_2 + \nu_1$ (D) All of these
45. The first Lyman transition in the hydrogen spectrum has $\Delta E = 10.2 \text{ eV}$. The same energy change is observed in the second Balmer transition of :-
 (A) Li^{2+} (B) Li^+ (C) He^+ (D) Be^{3+}
46. In a sample of H-atoms, electron transits from 6^{th} orbit to 2^{nd} orbit in multi step. Then total spectral lines (without Balmer series) will be :-
 (A) 6 (B) 10 (C) 4 (D) 0

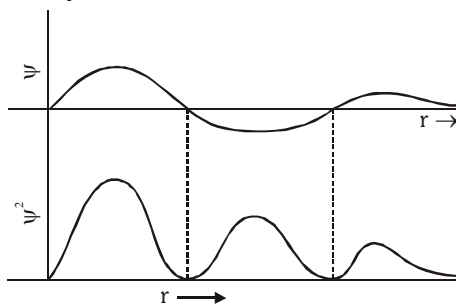
47. What is the shortest wavelength in the Pfund series of He^+ ion :-
 (A) $\frac{25}{R}$ (B) $\frac{4}{R}$ (C) $\frac{4R}{25}$ (D) $\frac{25}{4R}$
48. The shortest wavelength of He^+ ion in Balmer series is x , then longest wavelength in the Paschene series of Li^{+2} is
 (A) $\frac{36x}{5}$ (B) $\frac{16x}{7}$ (C) $\frac{9x}{5}$ (D) $\frac{5x}{9}$
49. The ratio of wave length of photon corresponding to the α -line of Lyman series in H-atom and β -line of Balmer series in He^+ is
 (A) 1 : 1 (B) 1 : 2 (C) 1 : 4 (D) 3 : 16
50. Three energy levels P, Q, R of a certain atom are such that $E_P < E_Q < E_R$. If λ_1, λ_2 and λ_3 are the wave length of radiation corresponding to transition $R \rightarrow Q$; $Q \rightarrow P$ and $R \rightarrow P$ respectively. The correct relationship between λ_1, λ_2 and λ_3 is
 (A) $\lambda_1 + \lambda_2 = \lambda_3$ (B) $\frac{1}{\lambda_3} = \frac{1}{\lambda_1} + \frac{1}{\lambda_2}$ (C) $\lambda_3 = \sqrt{\lambda_1 \lambda_2}$ (D) $\frac{2}{\lambda_3} = \frac{1}{\lambda_1} + \frac{1}{\lambda_2}$
51. Number of possible spectral lines which may be emitted in bracket series in H atom, if electrons present in 9th excited level returns to ground level, are
 (A) 21 (B) 6 (C) 45 (D) 5
52. The value of $(n_2 + n_1)$ and $(n_2^2 - n_1^2)$ for He^+ ion in atomic spectrum are 4 and 8 respectively. The wavelength of emitted photon when electron jump from n_2 to n_1 is
 (A) $\frac{32}{9} R_H$ (B) $\frac{9}{32} R_H$ (C) $\frac{9}{32 R_H}$ (D) $\frac{32}{9 R_H}$
53. An electron, a proton and an alpha particle have kinetic energies of 16E, 4E and E respectively. What is the qualitative order of their de Broglie wavelengths?
 (A) $\lambda_e > \lambda_p = \lambda_\alpha$ (B) $\lambda_p = \lambda_\alpha > \lambda_e$ (C) $\lambda_p > \lambda_e > \lambda_\alpha$ (D) $\lambda_\alpha < \lambda_e \gg \lambda_p$
54. The wavelength associated with a golf weighing 200g and moving at a speed of 5m/h is of the order
 (A) 10^{-10}m (B) 10^{-20}m (C) 10^{-30}m (D) 10^{-40}m
55. An electron has kinetic energy $2.8 \times 10^{-23} \text{ J}$. de-Broglie wavelength will be nearly :-
 ($m_e = 9.1 \times 10^{-31} \text{ kg}$)
 (A) $9.28 \times 10^{-24} \text{ m}$ (B) $9.28 \times 10^{-7} \text{ m}$ (C) $9.28 \times 10^{-8} \text{ m}$ (D) $9.28 \times 10^{-10} \text{ m}$
56. What will be de-Broglie wavelength of an electron moving with a velocity of $1.2 \times 10^5 \text{ ms}^{-1}$:-
 (A) $6.068 \times 10^{-9} \text{ m}$ (B) $3.133 \times 10^{-37} \text{ m}$ (C) $6.626 \times 10^{-9} \text{ m}$ (D) $6.018 \times 10^{-7} \text{ m}$
57. For a valid Bohr orbit, its circumference should be:
 (A) $= n \lambda$ (B) $= (n - 1) \lambda$ (C) $> n \lambda$ (D) $< n \lambda$
58. The number of waves made by a Bohr electron in an orbit of maximum magnetic quantum number + 2 :
 (A) 3 (B) 4 (C) 2 (D) 1
59. How fast is an electron moving if it has a wavelength equal to distance travelled in one second -
 (A) $\sqrt{\frac{m}{h}}$ (B) $\sqrt{\frac{h}{m}}$ (C) $\sqrt{\frac{h}{p}}$ (D) $\sqrt{\frac{h}{2 \times \text{K.E.}}}$

60. De-Broglie wavelength of two particles A & B are plotted against $\left(\frac{1}{\sqrt{V}}\right)$; where V is potential on the particles. Which of the following relation is correct about mass of particle (charge is same)
- (A) $M_A = M_B$
 (B) $M_A > M_B$
 (C) $M_A < M_B$
 (D) $M_A \leq M_B$
61. An α -particle is accelerated through a potential difference of V volts from rest. The de-Broglie's wavelength associated with it is -
- (A) $\sqrt{\frac{150}{V}} \text{Å}$ (B) $\frac{0.286}{\sqrt{V}} \text{Å}$ (C) $\frac{0.101}{\sqrt{V}} \text{Å}$ (D) $\frac{0.983}{\sqrt{V}} \text{Å}$
62. Which quantum number is not related with Schrodinger equation
- (A) Principal (B) Azimuthal (C) Magnetic (D) Spin
63. Which is true about ψ :-
- (A) ψ represents the probability of finding an electron around the nucleus
 (B) ψ represent the amplitude of the electron wave
 (C) Both A and B
 (D) None of these
64. According to Schrodinger model nature of electron in an atom is as :-
- (A) Particles only (B) Wave only
 (C) Both simultaneously (D) Sometimes waves and sometimes particle
65. The orbital angular momentum of an electron in 2s orbital is:
- (A) $+\frac{1}{2} \cdot \frac{h}{2\pi}$ (B) Zero (C) $\frac{h}{2\pi}$ (D) $\sqrt{2} \cdot \frac{h}{2\pi}$
66. In an excited state, a calcium atom has the electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 4d^1$. What is the orbital angular momentum for d electron :- $\left(\hbar = \frac{h}{2\pi}\right)$
- (A) $\sqrt{4}\hbar$ (B) $\sqrt{16}\hbar$ (C) $\sqrt{6}\hbar$ (D) $\sqrt{10}\hbar$
67. Which orbital has two angular nodal planes :-
- (A) s (B) p (C) d (D) f
68. From the following observations predict the type of orbital :
- Observation 1 : x y plane acts as nodal plane
 Observation 2 : The angular function of the orbital intersect the three axis at origin only.
 Observation 3 : $R^2(r)$ v/s r curve is obtained for the orbital is



- (A) $5p_z$ (B) $6d_{xy}$ (C) $6d_{x^2-y^2}$ (D) $6d_{yz}$

69. The wave function ψ vs radial distance (r) and square of wave function (ψ^2) vs radial distance (r) graph of certain orbital is given. Identify the orbital.



- (A) 3s (B) 4d (C) 3p (D) 4p
70. The distance of spherical nodes from nucleus for the given orbital are

$$\psi_{\text{radial}} = \frac{1}{9\sqrt{2}} \left(\frac{Z}{a_0} \right)^{3/2} [\sigma^2 - 4\sigma + 3] \exp(-\sigma/2)$$

where a_0 & Z are the constants and $\sigma = \frac{2Zr}{a_0}$

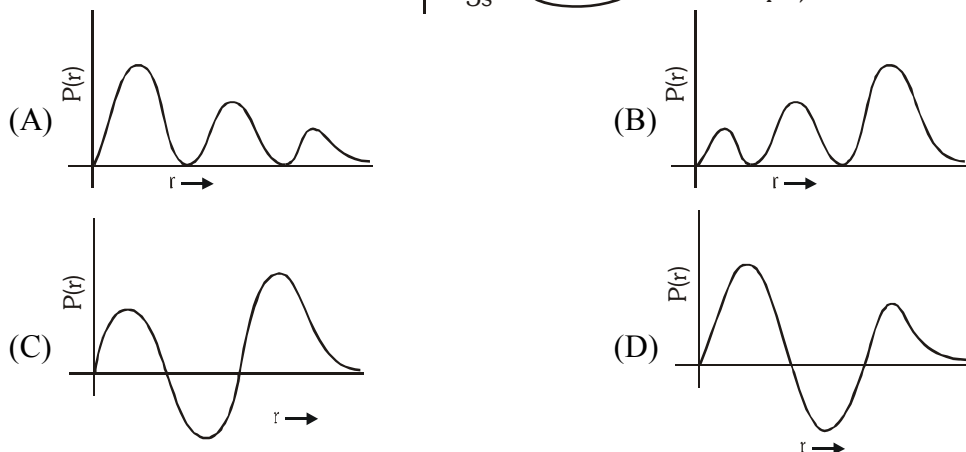
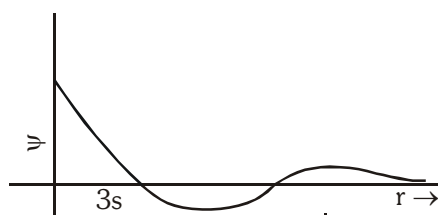
- (A) Zero, infinity (B) $\frac{a_0}{Z}, \frac{1}{2} \frac{a_0}{Z}$ (C) $\frac{3}{2} \frac{a_0}{Z}, \frac{1}{2} \frac{a_0}{Z}$ (D) $\frac{a_0}{Z}, \frac{3}{2} \frac{a_0}{Z}$

71. The radial function for an orbitals is :

$$R(r) = \frac{1}{9\sqrt{6}} \left(\frac{1}{a_0} \right) \cdot (4 - \sigma) \sigma e^{-\frac{\sigma}{3}}; \sigma = \frac{r}{a_0}$$

Pick out the incorrect statement :

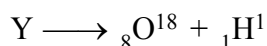
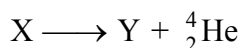
- (A) orbital must be 3p (B) orbital must be $3p_x$
 (C) the orbital has one radial node (D) the orbital must have one angular node
72. The wave function (ψ) verses radial distance (r) curve for certain orbital is given. Predict the shape of $\psi^2 \cdot 4\pi r^2$ (radial probability distribution function) verses r graph.



EXERCISE # O-II

SINGLE CORRECT :

- In a hydrogen like sample electron is in 2nd excited state, the energy of 4th state of this sample is -13.6 eV, then incorrect statement is :
 (A) Atomic number of element is 4.
 (B) 3 different types of spectral line will be observed if electrons make transition upto ground state from the 2nd excited state.
 (C) A 25 eV photon can set free the electron from the 2nd excited state of this sample
 (D) 2nd line of Balmer series of this sample has same energy value as 1st excitation energy of H-atoms.
- An electron in a hydrogen atom in its ground state absorbs energy equal to the ionisation energy of Li²⁺. The wavelength of the emitted electron is:
 (A) 3.32×10^{-10} m (B) 1.17 Å (C) 2.32×10^{-9} nm (D) 3.33 pm
- Given ΔH for the process $\text{Li(g)} \longrightarrow \text{Li}^{+3}(\text{g}) + 3\text{e}^-$ is 19800 kJ/mole & IE₁ for Li is 520 then IE₂ & IE₃ of Li are respectively (approx, value)
 (A) 7505, 11775 (B) 520, 19280 (C) 11775, 19280 (D) Data insufficient
- Consider the following nuclear reactions involving X & Y.



If both neutrons as well as protons in both the sides are conserved in nuclear reaction then moles of neutrons in 4.6 gm of X

- (A) $2.4 N_A$ (B) 2.4 (C) 4.6 (D) $0.2 N_A$

Assertion and Reason :

- Statement-1:** Energy emitted when an electron jump from 5 \rightarrow 2 (energy level) is less than when an electron jump from 2 \rightarrow 1 in all 'H' like atom.
Statement-2: The |total energy difference| between 1st & 2nd energy level is greater than that of any two energy level provided level '1' is not part of those two energy levels.
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
 (C) Statement-1 is true, statement-2 is false.
 (D) Statement-1 is false, statement-2 is true.
- Statement-1:** Emitted radiations will fall in visible range when an electron jump from higher level to $n=2$ in Li²⁺ ion.
Statement-2: Balmer series radiations belong to visible range in all H-atoms.
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
 (C) Statement-1 is true, statement-2 is false.
 (D) Statement-1 is false, statement-2 is true.

More than one may be correct :

7. Which of the following could be derived from Rutherford's α -particle scattering experiment-
 - (A) Most of the space in the atom is empty
 - (B) The radius of the atom is about 10^{-10} m while that of nucleus is 10^{-15} m
 - (C) Electrons move in a circular path of fixed energy called orbits
 - (D) Electrons and the nucleus are held together by electrostatic forces of attraction.
8. In a H-like sample electrons make transition from 5th excited state to 2nd excited state
 - (A) 10 different spectral lines will be emitted
 - (B) 6 different spectral lines will be emitted
 - (C) Number of lines belonging to Balmer series will be 4
 - (D) Number of lines belonging to paschen series will be 3
9. The kinetic energy of photoelectron emitted on irradiating a metal surface with frequency ν is related by $KE = h\nu - \phi$. The plots of KE vs. incident frequency ν shows :
 - (A) A straight line with slope equal to Planck's constant.
 - (B) A straight line with intercept on x-axis equal to the product of threshold frequency and Plank's constant.
 - (C) A straight line with extrapolated intercept on y-axis equal to threshold energy.
 - (D) A straight line with intercept on x-axis equal to threshold frequency.
10. Select the correct statement(s):
 - (A) All electromagnetic radiation travel with speed of light in vacuum.
 - (B) Energy of photon of UV light is lower than that of yellow light.
 - (C) He^+ and H have similar spectrum.
 - (D) The total energy of an electron in unielectronic specie is greater than zero
11. Choose the incorrect statement(s):
 - (A) Increasing order of wavelength is
Micro waves > Radio waves > IR waves > visible waves > UV waves
 - (B) The order of Bohr radius is (r_n : where n is orbit number for a given atom) $r_1 < r_2 < r_3 < r_4$
 - (C) The order of total energy is (E_n : where n is orbit number for a given atom) $E_1 > E_2 > E_3 > E_4$
 - (D) The order of velocity of electron in H, He^+ , Li^+ , Be^{3+} species in second Bohr orbit is
 $Be^{3+} > Li^{+2} > He^+ > H$

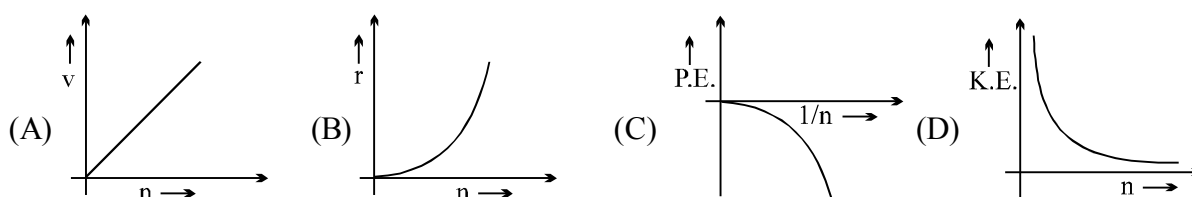
12. Select the correct curve(s):

If v = velocity of electron in Bohr's orbit

r = Radius of electron in Bohr's orbit

P.E. = Potential energy of electron in Bohr's orbit

K.E. = Kinetic energy of electron in Bohr's orbit.



13. Which is / are correct statement.

(A) The difference in angular momentum associated with the electron present in consecutive orbits of

$$\text{H-atom is } (n-1) \frac{h}{2\pi}$$

(B) Energy difference between energy levels will be changed if, P.E. at infinity assigned value other than zero.

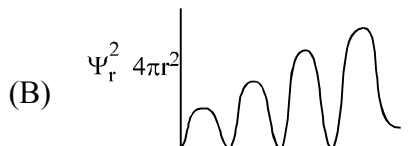
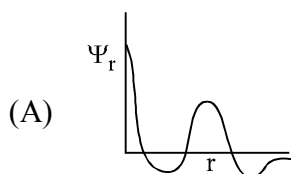
(C) Frequency of spectral line in a H-atom is in the order of $(2 \rightarrow 1) < (3 \rightarrow 1) < (4 \rightarrow 1)$

(D) On moving away from the nucleus, kinetic energy of electron decreases.

MATCH THE COLUMN :

14. Column I & column II contain data on Schrodinger Wave-Mechanical model, where symbols have their usual meanings. Match the columns.

Column I



(C) $\Psi(\theta, \phi) = K$ (independent of θ & ϕ)

(D) at least one angular node is present

Column II (Type of orbital)

(P) 4s

(Q) 5p_x

(R) 3s

(S) 6d_{xy}

15. **Column-I**

(A) Electron moving in 2nd orbit in He⁺ ion electron is

(B) Electron moving in 3rd orbit in H-atom

(C) Electron moving in 1st orbit in Li⁺² ion

(D) Electron moving in 2nd orbit is Be⁺³ ion

Column-II

(P) Radius of orbit in which moving is 0.529 Å

(Q) Total energy of electron is $(-13.6 \times 9 \text{ eV})$

(R) Velocity of electron is $\frac{2.188 \times 10^6}{3} \text{ m/sec}$

(S) De-broglie wavelength of

$$\text{electron is } \sqrt{\frac{150}{13.6}} \text{ Å}$$

COMPREHENSION :

Question No. 16 to 18 (3 questions)

The French physicist Louis de Broglie in 1924 postulated that matter, like radiation, should exhibit a dual behaviour. He proposed the following relationship between the wavelength λ of a material particle, its linear momentum p and planck constant h .

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

The de Broglie relation implies that the wavelength of a particle should decrease as its velocity increases. It also implies that for a given velocity heavier particles should have shorter wavelength than lighter particles. The waves associated with particles in motion are called matter waves or de Broglie waves. These waves differ from the electromagnetic waves as they

- (i) have lower velocities
- (ii) have no electrical and magnetic fields and
- (iii) are not emitted by the particle under consideration.

The experimental confirmation of the de Broglie relation was obtained when Davisson and Germer, in 1927, observed that a beam of electrons is diffracted by a nickel crystal. As diffraction is a characteristic property of waves, hence the beam of electron behaves as a wave, as proposed by de Broglie.

Werner Heisenberg considered the limits of how precisely we can measure properties of an electron or other microscopic particle like electron. He determined that there is a fundamental limit of how closely we can measure both position and momentum. The more accurately we measure the momentum of a particle, the less accurately we can determine its position. The converse is also true. This is summed up in what we now call the "Heisenberg uncertainty principle: It is impossible to determine simultaneously and precisely both the momentum and position of a particle. The product of uncertainty in the position,

Δx and the uncertainty in the momentum $\Delta(mv)$ must be greater than or equal to $\frac{h}{4\pi}$. i.e.

$$\Delta x \Delta(mv) \geq \frac{h}{4\pi}$$

16. The correct order of wavelength of Hydrogen (${}_1H^1$), Deuterium (${}_1H^2$) and Tritium (${}_1H^3$) moving with same kinetic energy is
 (A) $\lambda_H > \lambda_D > \lambda_T$ (B) $\lambda_H = \lambda_D = \lambda_T$ (C) $\lambda_H < \lambda_D < \lambda_T$ (D) $\lambda_H < \lambda_D > \lambda_T$
17. The transition, so that the de-Broglie wavelength of electron becomes 3 times of its initial value in He^+ ion will be
 (A) $2 \rightarrow 5$ (B) $3 \rightarrow 2$ (C) $2 \rightarrow 6$ (D) $1 \rightarrow 2$
18. If the uncertainty in velocity & position is same, then the uncertainty in momentum will be
 (A) $\sqrt{\frac{hm}{4\pi}}$ (B) $m\sqrt{\frac{h}{4\pi}}$ (C) $\sqrt{\frac{h}{4\pi m}}$ (D) $\frac{1}{m}\sqrt{\frac{h}{4\pi}}$

Question No. 19 to 22 (4 questions)

The only electron in the hydrogen atom resides under ordinary conditions on the first orbit. When energy is supplied, the electron moves to higher energy orbit depending on the amount of energy absorbed. When this electron returns to any of the lower orbits, it emits energy. Lyman series is formed when the electron returns to the lowest orbit while Balmer series is formed when the electron returns to second orbit. Similarly, Paschen, Brackett and Pfund series are formed when electron returns to the third, fourth and fifth orbits from higher energy orbits respectively.

Maximum number of lines produced when an electron jumps from n th level to ground level is equal to $\frac{n(n-1)}{2}$. For example, in the case of $n = 4$, number of lines produced is 6. ($4 \rightarrow 3$, $4 \rightarrow 2$, $4 \rightarrow 1$, $3 \rightarrow 2$, $3 \rightarrow 1$, $2 \rightarrow 1$). When an electron returns from n_2 to n_1 state, the number of lines in the spectrum will be equal to

$$\frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$$

If the electron comes back from energy level having energy E_2 to energy level having energy E_1 , then the difference may be expressed in terms of energy of photon as:

$$E_2 - E_1 = \Delta E, \lambda = \frac{hc}{\Delta E}$$

Since h and c are constants, ΔE corresponds to definite energy; thus each transition from one energy level to another will produce a light of definite wavelength. This is actually observed as a line in the spectrum of hydrogen atom.

Wave number of line is given by the formula $\bar{\nu} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$.

where R is a Rydberg's constant ($R = 1.1 \times 10^7 \text{ m}^{-1}$)

19. The energy photon emitted corresponding to transition $n = 3$ to $n = 1$ is [$h = 6 \times 10^{-34} \text{ J-sec.}$]
 (A) $1.76 \times 10^{-18} \text{ J}$ (B) $1.98 \times 10^{-18} \text{ J}$ (C) $1.76 \times 10^{-17} \text{ J}$ (D) None of these
20. In a collection of H-atom, electrons make transition from 5th excited state to 2nd excited state then maximum number of different types of photons observed are
 (A) 3 (B) 4 (C) 6 (D) 15
21. The difference in the wavelength of the 1st line of Lyman series and 2nd line of Balmer series in a hydrogen atom is
 (A) $\frac{9}{2R}$ (B) $\frac{4}{R}$ (C) $\frac{88}{15R}$ (D) None
22. The wave number of electromagnetic radiation emitted during the transition of electron in between two levels of Li^{2+} ion whose principal quantum numbers sum is 4 and difference is 2 is
 (A) $3.5 R$ (B) $4 R$ (C) $8 R$ (D) $\frac{8}{9} R$

1 TABLE (3Q)

Column-I	Column-II	Column-III
(A) Energy of electron in H-like atomic orbital	(P) Principal quantum number(n)	(I) Radial function [R(r)]
(B) Orientation and shape of H-like atomic orbital	(Q) Azimuthal quantum number (l)	(II) Angular function
(C) Magnitude & direction of spin angular momentum	(R) Magnetic quantum number (m)	(III) Wave function [Ψ]
(D) Probability density of electron in s-orbital of H-like atom/ion	(S) Spin quantum number(s)	(IV) Cannot be determined from Schrodinger equation

Assume no external electric or magnetic fields in Q.25 to Q.26

23. Which of the following option is incorrectly matched -
 (A) B – Q – II (B) B – R – II (C) B – P – I (D) B – Q – III
24. Which option is correctly matched ?
 (A) C – S – III (B) D – R – III (C) A – P – IV (D) C – S – IV
25. If option (A) is considered in presence of external electric or magnetic field then which option is incorrect -
 (A) A – P – III (B) A – Q – III (C) A – R – III (D) A – S – I

EXERCISE # J-MAINS

- An atom has a mass of 0.02 kg and uncertainty in its velocity is 9.218×10^{-6} m/s then uncertainty in position is ($h = 6.626 \times 10^{-34}$ Js) [AIEEE 2002]
 (1) 2.86×10^{-28} m (2) 2.86×10^{-32} cm (3) 1.5×10^{-27} m (4) 3.9×10^{-10} m
- Energy of H- atom in the ground state is -13.6 eV, Hence energy in the second excited state is- [AIEEE 2002]
 (1) -6.8 eV (2) -3.4 eV (3) -1.51 eV (4) -4.3 eV
- Uncertainty in position of a particle of 25 g in space is 10^{-5} m. Hence uncertainty in velocity (ms^{-1}) is (Planck's constant $h = 6.6 \times 10^{-34}$ Js) [AIEEE-2002]
 (1) 2.1×10^{-28} (2) 2.1×10^{-34} (3) 0.5×10^{-34} (4) 5.0×10^{-24}
- The orbital angular momentum for an electron revolving in an orbit is given by $\sqrt{\ell(\ell+1)} \cdot \frac{h}{2\pi}$. This momentum for an s-electron will be given by [AIEEE-2003]
 (1) $\sqrt{2} \cdot \frac{h}{2\pi}$ (2) $+\frac{1}{2} \cdot \frac{h}{2\pi}$ (3) zero (4) $\frac{h}{2\pi}$
- The number of d-electrons retained in Fe^{2+} (At. no. of Fe = 26) ion is : [AIEEE-2003]
 (1) 6 (2) 3 (3) 4 (4) 5
- The de Broglie wavelength of a tennis ball of mass 60 g moving with a velocity of 10 metres per second is approximately : [AIEEE 2003]
 (1) 10^{-25} metres (2) 10^{-33} metres (3) 10^{-31} metres (4) 10^{-16} metres
- In Balmer series of lines of hydrogen spectrum, the third line from the red end corresponds to which one of the following inter-orbit jumps of the electron for Bohr orbits in an atom of hydrogen ? [AIEEE-2003]
 (1) $2 \rightarrow 5$ (2) $3 \rightarrow 2$ (3) $5 \rightarrow 2$ (4) $4 \rightarrow 1$
- Which of the following sets of quantum number is correct for an electron in 4f orbital ? [AIEEE-2004]
 (1) $n = 3, l = 2, m = -2, s = +\frac{1}{2}$ (2) $n = 4, l = 4, m = -4, s = -\frac{1}{2}$
 (3) $n = 4, l = 3, m = +1, s = +\frac{1}{2}$ (4) $n = 4, l = 3, m = +4, s = +\frac{1}{2}$
- The wavelength of the radiation emitted, when in a hydrogen atom electron falls from infinity to stationary state 1, would be [AIEEE-2004]
 (Rydberg constant = $1.097 \times 10^7 \text{ m}^{-1}$) :
 (1) 9.1×10^{-8} nm (2) 192 nm (3) 406 nm (4) 91 nm
- Which of the following statements in relation to the hydrogen atom is correct ? [AIEEE-2005]
 (1) 3s, 3p and 3d orbitals all have the same energy
 (2) 3s and 3p orbitals are of lower energy than 3d orbitals
 (3) 3p orbital is lower in energy than 3d orbital
 (4) 3s orbitals is lower in energy than 3p orbital

11. According to Bohr's theory angular momentum of electron in 5th shell is :- [AIEEE-2006]
 (1) $1.0 \text{ h}/\pi$ (2) $10 \text{ h}/\pi$ (3) $2.5 \text{ h}/\pi$ (4) $25 \text{ h}/\pi$
12. Uncertainty in the position of an electron (mass = $9.1 \times 10^{-31} \text{ Kg}$) moving with a velocity 300 ms^{-1} , accurate upto 0.001%, will be :- ($h = 6.63 \times 10^{-34} \text{ Js}$) [AIEEE-2006]
 (1) $5.76 \times 10^{-2} \text{ m}$ (2) $1.92 \times 10^{-2} \text{ m}$ (3) $3.84 \times 10^{-2} \text{ m}$ (4) $19.2 \times 10^{-2} \text{ m}$
13. The ionization enthalpy of hydrogen atom is $1.312 \times 10^6 \text{ J mol}^{-1}$. The energy required to excite the electron in the atom from $n=1$ to $n=2$ is [AIEEE-2008]
 (1) $8.51 \times 10^5 \text{ J mol}^{-1}$ (2) $6.56 \times 10^5 \text{ J mol}^{-1}$ (3) $7.56 \times 10^5 \text{ J mol}^{-1}$ (4) $9.84 \times 10^5 \text{ J mol}^{-1}$
14. In an atom, an electron is moving with a speed of 600 m/s with an accuracy of 0.005%. Certainty with which the position of the electron can be located is ($h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}$, mass of electron, $m_e = 9.1 \times 10^{-31} \text{ kg}$):- [AIEEE-2009]
 (1) $1.92 \times 10^{-3} \text{ m}$ (2) $3.84 \times 10^{-3} \text{ m}$ (3) $1.52 \times 10^{-4} \text{ m}$ (4) $5.10 \times 10^{-3} \text{ m}$
15. Calculate the wavelength (in nanometer) associated with a proton moving at $1.0 \times 10^3 \text{ ms}^{-1}$ (Mass of proton = $1.67 \times 10^{-27} \text{ kg}$ and $h = 6.63 \times 10^{-34} \text{ Js}$) :- [AIEEE-2009]
 (1) 2.5 nm (2) 14.0 nm (3) 0.032 nm (4) 0.40 nm
16. The energy required to break one mole of Cl-Cl bonds in Cl_2 is 242 kJ mol^{-1} . The longest wavelength of light capable of breaking a single Cl-Cl bond is ($C = 3 \times 10^8 \text{ ms}^{-1}$ and $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$) [AIEEE-2010]
 (1) 494 nm (2) 594 nm (3) 640 nm (4) 700 nm
17. Ionisation energy of He^+ is $19.6 \times 10^{-18} \text{ J atom}^{-1}$. The energy of the first stationary state ($n=1$) of Li^{2+} is:- [AIEEE-2010]
 (1) $8.82 \times 10^{-17} \text{ J atom}^{-1}$ (2) $4.41 \times 10^{-16} \text{ J atom}^{-1}$
 (3) $-4.41 \times 10^{-17} \text{ J atom}^{-1}$ (4) $-2.2 \times 10^{-15} \text{ J atom}^{-1}$
18. A gas absorbs a photon of 355 nm and emits at two wavelengths. If one of the emissions is at 680 nm, the other is at :- [AIEEE-2011]
 (1) 743 nm (2) 518 nm (3) 1035 nm (4) 325 nm
19. The frequency of light emitted for the transition $n=4$ to $n=2$ of He^+ is equal to the transition in H atom corresponding to which of the following [AIEEE-2011]
 (1) $n=3$ to $n=1$ (2) $n=2$ to $n=1$ (3) $n=3$ to $n=2$ (4) $n=4$ to $n=3$
20. The electrons identified by quantum numbers n and ℓ :- [AIEEE-2012]
 (a) $n=4, \ell=1$ (b) $n=4, \ell=0$ (c) $n=3, \ell=2$ (d) $n=3, \ell=1$
 Can be placed in order of increasing energy as
 (1) (a) < (c) < (b) < (d) (2) (c) < (d) < (b) < (a)
 (3) (d) < (b) < (c) < (a) (4) (b) < (d) < (a) < (c)
21. If the kinetic energy of an electron is increased four times, the wavelength of the de-Broglie wave associated with it would become :- [JEE-Main(online) 2012]
 (1) Two times (2) Half (3) One fourth (4) Four times
22. If the radius of first orbit of H atom is a_0 , the de-Broglie wavelength of an electron in the third orbit is :- [JEE-Main(online) 2012]
 (1) $6 \pi a_0$ (2) $8 \pi a_0$ (3) $2 \pi a_0$ (4) $4 \pi a_0$

23. The wave number of the first emission line in the Balmer series of H-Spectrum is :
(R = Rydberg constant) : **[JEE-Main(online) 2013]**
- (1) $\frac{3}{4}R$ (2) $\frac{9}{400}R$ (3) $\frac{5}{36}R$ (4) $\frac{7}{6}R$
24. The de Broglie wavelength of a car of mass 1000 kg and velocity 36 km/hr is :
($h = 6.63 \times 10^{-34}$ Js) **[JEE-Main(online) 2013]**
- (1) 6.626×10^{-31} m (2) 6.626×10^{-34} m
(3) 6.626×10^{-38} m (4) 6.626×10^{-30} m
25. For which of the following particles will it be most difficult to experimentally verify the de-Broglie relationship? **[JEE-Main(online) 2014]**
- (1) a dust particle (2) an electron (3) a proton (4) an α -particle.
26. If the binding energy of the electron in a hydrogen atom is 13.6 eV, the energy required to remove the electron from the first excited state of Li^{++} is : **[JEE-Main(online) 2014]**
- (1) 13.6 eV (2) 30.6 eV (3) 122.4 eV (4) 3.4 eV
27. Based on the equation **[JEE-Main(online) 2014]**
- $$\Delta E = -2.0 \times 10^{-18} J \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right)$$
- the wavelength of the light that must be absorbed to excite hydrogen electron from level $n=1$ to level $n=2$ will be ($h = 6.625 \times 10^{-34}$ Js, $C = 3 \times 10^8$ ms $^{-1}$) **[JEE-Main(online) 2014]**
- (1) 2.650×10^{-7} m (2) 1.325×10^{-7} m
(3) 1.325×10^{-10} m (4) 5.300×10^{-10} m
28. If λ_0 and λ be the threshold wavelength and wavelength of incident light, the velocity of photoelectron ejected from the metal surface is **[JEE-Main(online) 2014]**
- (1) $\sqrt{\frac{2hc}{m} \left(\frac{\lambda_0 - \lambda}{\lambda \lambda_0} \right)}$ (2) $\sqrt{\frac{2h}{m} \left(\frac{1}{\lambda_0} - \frac{1}{\lambda} \right)}$ (3) $\sqrt{\frac{2h}{m} (\lambda_0 - \lambda)}$ (4) $\sqrt{\frac{2hc}{m} (\lambda_0 - \lambda)}$
29. Ionization energy of gaseous Na atoms is 495.5 kJmol $^{-1}$. The lowest possible frequency of light that ionizes a sodium atom is **[JEE-Main(online) 2014]**
- ($h = 6.626 \times 10^{-34}$ Js, $N_A = 6.022 \times 10^{23}$ mol $^{-1}$)
- (1) 3.15×10^{15} s $^{-1}$ (2) 4.76×10^{14} s $^{-1}$ (3) 1.24×10^{15} s $^{-1}$ (4) 7.50×10^4 s $^{-1}$
30. Which of the following is the energy of a possible excited state of hydrogen? **[JEE-Main(offline) 2015]**
- (1) -3.4 eV (2) +6.8 eV (3) +13.6 eV (4) -6.8 eV
31. At temperature T, the average kinetic energy of any particle is $\frac{3}{2}$ kT- The de Broglie wavelength follows the order : **[JEE-Main(online) 2015]**
- (1) Visible photon > Thermal electron > Thermal neutron
(2) Thermal proton > Thermal electron > Visible photon
(3) Visible photon > Thermal neutron > Thermal electron
(4) Thermal proton > Visible photon > Thermal electron

32. A stream of electrons from a heated filament was passed between two charged plates kept at a potential difference V volts. If e and m are charge and mass of an electron respectively, then the value of h/λ (where λ is wavelength associated with electron wave) is given by : [JEE-Main(online) 2016]
- (1) $\sqrt{2meV}$ (2) meV (3) $2meV$ (4) \sqrt{meV}
33. The radius of the second Bohr orbit for hydrogen atom is : [JEE-Main(offline) 2017]
- (Plank's const. $h = 6.6262 \times 10^{-34}$ Js ; mass of electron = 9.1091×10^{-31} kg ; charge of electron $e = 1.60210 \times 10^{-19}$ C ; permittivity of vacuum $\epsilon_0 = 8.854185 \times 10^{-12}$ kg⁻¹ m³ A²)
- (1) 1.65\AA (2) 4.76\AA (3) 0.529\AA (4) 2.12\AA
34. If the shortest wavelength in Lyman series of hydrogen atom is A , then the longest wavelength in Paschen series of He^+ is : [JEE-Main(online) 2017]
- (1) $\frac{36A}{5}$ (2) $\frac{9A}{5}$ (3) $\frac{36A}{7}$ (4) $\frac{5A}{9}$
35. The electron in the hydrogen atom undergoes transition from higher orbitals to orbital of radius 211.6 pm. This transition is associated with:- [JEE-Main(online) 2017]
- (1) Brackett series (2) Balmer series (3) Lyman series (4) Paschen series
36. The de-Broglie's wavelength of electron present in first Bohr orbit of 'H' atom is :- [JEE-Main(online) 2018]
- (1) $\frac{0.529}{2\pi}\text{\AA}$ (2) $2\pi \times 0.529\text{\AA}$ (3) 0.529\AA (4) $4 \times 0.529\text{\AA}$
37. Ejection of the photoelectron from metal in the photoelectric effect experiment can be stopped by applying 0.5 V when the radiation of 250 nm is used. The work function of the metal is : [JEE-Main(online) 2018]
- (1) 5 eV (2) 4 eV (3) 5.5 eV (4) 4.5 eV
38. Which of the following statements is false ? [JEE-Main(online) 2018]
- (1) Photon has momentum as well as wavelength.
 (2) Splitting of spectral lines in electrical field is called Stark effect.
 (3) Frequency of emitted radiation from a black body goes from a lower wavelength to higher wavelength as the temperature increases.
 (4) Rydberg constant has unit of energy.

EXERCISE # J-ADVANCE

- With what velocity should an α -particle travel towards the nucleus of a Cu atom so as to arrive at a distance 10^{-13} m. [JEE 1997]
- A compound of Vanadium has magnetic moment of 1.73 BM work out electronic configuration of Vanadium Ion in the compound. [JEE 1997]
- The energy of an electron in the first Bohr orbit of H atom is -13.6 eV. The possible energy value(s) of the excited state(s) for electrons in Bohr orbits of hydrogen is/are :
(A) -3.4 eV (B) -4.2 eV (C) -6.8 eV (D) $+6.8$ eV [JEE 1998]
- The number of nodal planes in a p_x orbital is: [JEE 2000]
(A) one (B) two (C) three (D) zero
- Calculate the energy required to excite one litre of hydrogen gas at 1 atm and 298K to the first excited state of atomic hydrogen. The energy for the dissociation of $H-H$ is 436 kJ mol $^{-1}$.
- The quantum numbers $+1/2$ and $-1/2$ for the electron spin represent: [JEE 2001]
(A) rotation of the electron in clockwise and anticlockwise direction respectively.
(B) rotation of the electron in anticlockwise and clockwise direction respectively.
(C) magnetic moment of the electron pointing up and down respectively.
(D) two quantum mechanical spin states which have no classical analogue.
- Rutherford's experiment, which established the nuclear model of atom, used a beam of :—
(A) β - particles, which impinged on a metal foil and get absorbed. [JEE 2002]
(B) γ - rays, which impinged on a metal foil and ejected electron.
(C) Helium atoms, which impinged on a metal foil and got scattered.
(D) Helium nuclei, which impinged on a metal foil and got scattered.
- The magnetic moment of cobalt of the compound $Hg[Co(SCN)_4]$ is [Given : Co^{+2}]
(A) $\sqrt{3}$ (B) $\sqrt{8}$ (C) $\sqrt{15}$ (D) $\sqrt{24}$ [JEE 2004]
- The radius of which of the following orbit is same as that of the first Bohr's orbit of hydrogen atom?
(A) He^+ ($n=2$) (B) Li^{2+} ($n=2$) (C) Li^{2+} ($n=3$) (D) Be^{3+} ($n=2$) [JEE 2004]
- (a) The Schrodinger wave equation for hydrogen atom is [IIT-2004]

$$\psi_{2s} = \frac{1}{4(2\pi)^{1/2}} \left(\frac{1}{a_0} \right)^{3/2} \left(2 - \frac{r_0}{a_0} \right) e^{-r/a}$$

Where a_0 is Bohr's radius. Let the radial node in 2s be at r_0 . Then find r_0 in terms of a_0 .
 (b) A baseball having mass 100 g moves with velocity 100 m/s. Find out the value of wavelength of baseball.
- (a) Calculate velocity of electron in first Bohr orbit of hydrogen atom (Given $r = a_0$) [IIT-2005]
 (b) Find de-Broglie wavelength of the electron in first Bohr orbit.
 (c) Find the orbital angular momentum of 2p-orbital in terms of $h/2\pi$ units.

12. Given in hydrogenic atom r_n , V_n , E , K_n stand for radius, potential energy, total energy and kinetic energy in n^{th} orbit. Find the value of U, v, x, y . [JEE 2006]

(A) $U = \frac{V_n}{K_n}$ (P) 1

(B) $\frac{1}{r_n} \propto E^x$ (Q) -2

(C) $r_n \propto Z^y$ (R) -1
(Z = Atomic number)

(D) v = (Orbital angular momentum of electron in its lowest energy) (S) 0

13. Match the entries in **Column I** with the correctly related quantum number(s) in **Column II**. Indicate your answer by darkening the appropriate bubbles of the 4×4 matrix given in the ORS.

[JEE 2008]

Column I

- (A) Orbital angular momentum of the electron in a hydrogen-like atomic orbital
(B) A hydrogen-like one-electron wave function obeying Pauli principle
(C) Shape, size and orientation of hydrogen like atomic orbitals
(D) Probability density of electron at the nucleus in hydrogen-like atom

Column II

- (P) Principal quantum number
(Q) Azimuthal quantum number
(R) Magnetic quantum number
(S) Electron spin quantum number

Paragraph for questions 14 to 16

[JEE 2010]

The hydrogen-like species Li^{2+} is in a spherically symmetric state S_1 with one radial node. Upon absorbing light the ion undergoes transition to a state S_2 . The state S_2 has one radial node and its energy is equal to the ground state energy of the hydrogen atom.

14. The state S_1 is :-

- (A) 1s (B) 2s (C) 2p (D) 3s

15. Energy of the state S_1 in units of the hydrogen atom ground state energy is :-

- (A) 0.75 (B) 1.50 (C) 2.25 (D) 4.50

16. The orbital angular momentum quantum number of the state S_2 is :-

- (A) 0 (B) 1 (C) 2 (D) 3

17. The maximum number of electrons that can have principal quantum number, $n=3$, and spin quantum number, $m_s = -1/2$, is [JEE 2011]

18. The work function (ϕ) of some metals is listed below. The number of metals which will show photoelectric effect when light of 300 nm wavelength falls on the metal is :- [JEE 2011]

Metal	Li	Na	K	Mg	Cu	Ag	Fe	Pt	W
ϕ (eV)	2.4	2.3	2.2	3.7	4.8	4.3	4.7	6.3	4.75

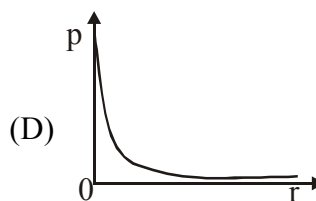
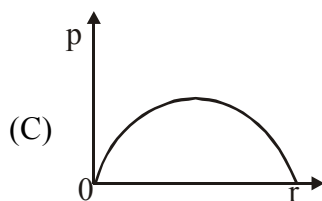
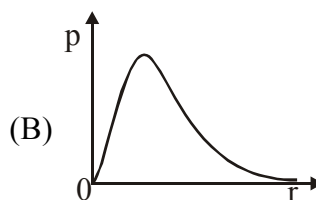
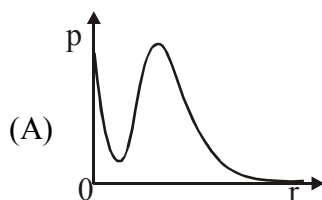
19. The kinetic energy of an electron in the second Bohr orbit of a hydrogen atom is [a_0 is Bohr radius] [JEE 2012]

(A) $\frac{h^2}{4\pi^2ma_0^2}$ (B) $\frac{h^2}{16\pi^2ma_0^2}$ (C) $\frac{h^2}{32\pi^2ma_0^2}$ (D) $\frac{h^2}{32\pi^2ma_0^2}$

20. The atomic masses of He and Ne are 4 and 20 a.m.u. respectively. The value of the de Broglie wavelength of He gas at -73°C is "M" times that of the de Broglie wavelength of Ne at 727°C . M is. [JEE 2013]

21. In an atom, the total number of electrons having quantum numbers $n = 4$, $|m_l| = 1$ and $m_s = -\frac{1}{2}$ is [JEE 2014]

22. P is the probability of finding the 1s electron of hydrogen atom in a spherical shell of infinitesimal thickness, dr , at a distance r from the nucleus. The volume of this shell is $4\pi r^2 dr$. The qualitative sketch of the dependence of P on r is - [JEE 2016]



Answer Q.23, Q.24 and Q.25 by appropriately matching the information given in the three columns of the following table. [JEE 2017]

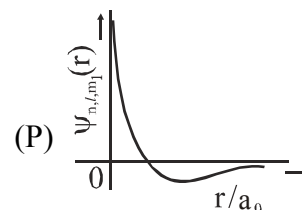
Column-1

Column-2

Column-3

(I) 1s orbital

$$(i) \psi_{n,l,m_l} \propto \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-\left(\frac{Zr}{a_0}\right)}$$



(II) 2s orbital

(ii) One radial node

(Q) Probability density at

$$\text{nucleus} \propto \frac{1}{a_0^3}$$

(III) 2p_z orbital

$$(iii) \psi_{n,l,m_l} \propto \left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r e^{-\left(\frac{Zr}{2a_0}\right)} \cos \theta$$

(R) Probability density is

maximum at nucleus

(IV) 3d_{z²} orbital

(iv) xy - plane is a nodal plane

(S) Energy needed to excite electron from n = 2 state to n = 4 state is $\frac{27}{32}$ times the energy needed to excite electron from n = 2 state to n = 6 state

23. For the given orbital in column 1, the only **CORRECT** combination for any hydrogen - like species is :

(A) (IV) (iv) (R) (B) (II) (ii) (P) (C) (III) (iii) (P) (D) (I) (ii) (S)

24. For He⁺ ion, the only **INCORRECT** combination is

(A) (II) (ii) (Q) (B) (I) (i) (S) (C) (I) (i) (R) (D) (I) (iii) (R)

25. For hydrogen atom, the only **CORRECT** combination is

(A) (I) (iv) (R) (B) (I) (i) (P) (C) (II) (i) (Q) (D) (I) (i) (S)

ANSWER KEY

EXERCISE # S-I

1. (1 : 1)
2. (4 : 9)
3. $n < \alpha < p < e$
4. 6.0×10^{-19} unit.
5. 1.6×10^{-19} Coulomb.
6. $8 \times 10^{-15} : 1$
7. $2.3 \times 10^{17} \text{ kg/m}^3$
8. 1 : 2
9. $1.28 \times 10^{-14} \text{ m}$.
10. $1.44 \times 10^7 \text{ m/s}$
11. 1500 Å
12. 150 KHz
13. 1 : 5
14. $7.5 \times 10^{12} \text{ Hz}$
15. $4.96 \times 10^{-19} \text{ Joule}$
16. 1.0×10^5
17. 10^{22}
18. 0.5
19. 6200 Å
20. 3×10^{22}
21. ($2 \times 10^{15} \text{ Hz}$, $1.5 \times 10^{-7} \text{ m}$)
22. (1)
23. 50 %
24. 3.06 V
25. Ans. 0.41375 eV
26. Ans.(0.2645) Å
27. Ans.(x = 4)
28. $5.44 \times 10^5 \text{ m/s}$
29. 2
30. 8×10^6
31. $6530 \times 10^{12} \text{ Hz}$
32. $-1.36 \times 10^{-19} \text{ Joules}$
33. h/π
34. (2)
35. 1.18×10^7
36. ($-217.9 \times 10^{-20} \text{ J}$)
37. 340 eV, - 680 eV
38. (6)
39. 6563 Å ; 1216 Å ; 1026 Å
40. 10.2 eV, z = 2
41. 113.74 Å
42. (i) $\frac{x}{4}$; (ii) $\frac{36x}{7}$
43. (3)
44. (4)
45. $3.09 \times 10^8 \text{ cm/sec}$
46. (3)
47. (8)
48. (4)
49. $3.68 \times 10^{-65} \text{ m}$
50. 10 pm
51. 0.0826 volts
52. $1.05 \times 10^{-13} \text{ m}$
53. (0.175 cm)
54. Ans (8)
56. $\frac{9+3\sqrt{3}}{2} a_0, \frac{9-3\sqrt{3}}{2} a_0$
57. (3)
58. (2)
59. (0.423 Å)
60. (4)

EXERCISE # S-II

1. (20)
2. $E = \frac{n^6 h^6}{384 m^3 K^2 e^4 \pi^6}$
3. (i) 1, (ii) 2, (iii) 3, (iv) 3
4. - 435.2 eV
5. (90 nm)
6. 91 nm
7. (a) $Z = 3$; (b) $n_1 = 12$, $n_2 = 15$; (c) $\lambda_{\max} = 15406 \text{ nm}$
8. $R \left(\frac{8}{9} \right)$
9. 973.5 Å
10. 303.89 Å , $2.645 \times 10^{-9} \text{ cm}$
11. (a) 75 eV ; (b) 1.414 Å ; (c) $2 \times 10^{-14} \text{ m}$
12. Ans. ($5 \times 10^{-26} \text{ m}$)
13. $3.63 \times 10^6 \text{ m}^{-1}$
14. Ans. (1240 kJ/mol.)
15. 300303

EXERCISE # O-I

- | | | |
|--------------|-------------|-------------|
| 1. Ans.(C) | 2. Ans.(C) | 3. Ans.(C) |
| 4. Ans.(C) | 5. Ans.(A) | 6. Ans.(D) |
| 7. Ans.(D) | 8. Ans.(D) | 9. Ans.(D) |
| 10. Ans.(C) | 11. Ans.(A) | 12. Ans.(D) |
| 13. Ans.(B) | 14. Ans.(B) | 15. Ans.(B) |
| 16. Ans.(B) | 17. Ans.(B) | 18. Ans.(C) |
| 19. Ans. (A) | 20. Ans.(C) | 21. Ans.(A) |
| 22. Ans.(B) | 23. Ans.(A) | 24. Ans.(B) |
| 25. Ans.(B) | 26. Ans.(A) | 27. Ans.(C) |
| 28. Ans.(C) | 29. Ans.(A) | 30. Ans.(D) |
| 31. Ans.(A) | 32. Ans.(C) | 33. Ans.(B) |
| 34. Ans.(D) | 35. Ans.(C) | 36. Ans.(B) |
| 37. Ans.(C) | 38. Ans.(D) | 39. Ans.(A) |
| 40. Ans.(C) | 41. Ans.(A) | 42. Ans.(D) |
| 43. Ans.(B) | 44. Ans.(C) | 45. Ans.(C) |
| 46. Ans.(A) | 47. Ans.(D) | 48. Ans.(B) |
| 49. Ans.(A) | 50. Ans.(B) | 51. Ans.(B) |
| 52. Ans.(C) | 53. Ans.(A) | 54. Ans.(C) |
| 55. Ans.(C) | 56. Ans.(A) | 57. Ans.(A) |
| 58. Ans.(A) | 59. Ans.(B) | 60. Ans.(B) |
| 61. Ans.(C) | 62. Ans.(D) | 63. Ans.(B) |
| 64. Ans.(C) | 65. Ans.(B) | 66. Ans.(C) |
| 67. Ans.(C) | 68. Ans.(D) | 69. Ans.(D) |
| 70. Ans.(C). | 71. Ans.(B) | 72. Ans.(B) |

EXERCISE # O-II

- | | | |
|---|---------------|------------------|
| 1. Ans.(D) | 2. Ans.(B) | 3. Ans.(A) |
| 4. Ans.(B) | 5. Ans.(A) | 6. Ans.(D) |
| 7. Ans.(A,B,D) | 8. Ans.(B,D) | 9. Ans. (A,D) |
| 10. Ans.(A,C) | 11. Ans.(A,C) | 12. Ans. (B,C,D) |
| 13. Ans.(C,D) | | |
| 14. Ans.(A)-P ; (B)-P,Q,S ; (C)-P,R ; (D)-Q,S | | |
| 15. Ans.(A)-S ; (B)-R ; (C)-Q ; (D)-P | | |
| 16. Ans.(A) | 17. Ans.(C) | 18. Ans.(A) |
| 19. Ans.(A) | 20. Ans.(C) | 21. Ans.(B) |
| 22. Ans.(C) | 23. Ans.(C) | 24. Ans.(D) |
| 25. Ans.(D) | | |

EXERCISE # J-MAINS

- | | | |
|-------------|-------------|-------------|
| 1. Ans.(1) | 2. Ans.(3) | 3. Ans.(1) |
| 4. Ans.(3) | 5. Ans.(1) | 6. Ans.(2) |
| 7. Ans.(3) | 8. Ans.(3) | 9. Ans.(4) |
| 10. Ans.(1) | 11. Ans.(3) | 12. Ans.(2) |
| 13. Ans.(4) | 14. Ans.(1) | 15. Ans.(4) |
| 16. Ans.(1) | 17. Ans.(3) | 18. Ans.(1) |
| 19. Ans.(2) | 20. Ans.(3) | 21. Ans.(2) |
| 22. Ans.(1) | 23. Ans.(3) | 24. Ans.(3) |
| 25. Ans.(1) | 26. Ans.(2) | 27. Ans.(2) |
| 28. Ans.(1) | 29. Ans.(3) | 30. Ans.(1) |
| 31. Ans.(1) | 32. Ans.(1) | 33. Ans.(4) |
| 34. Ans.(3) | 35. Ans.(2) | 36. Ans.(2) |
| 37. Ans.(4) | 38. Ans.(3) | |

EXERCISE #J-ADVANCE

- | | | |
|---|-------------------------------------|--------------|
| 1. Ans. 6.3×10^6 m/s | 2. Ans. [Ar] $3d^1$ | 3. Ans. (A) |
| 4. Ans. (A) | 5. Ans. 97.819 KJ | 6. Ans. (D) |
| 7. Ans. (D) | 8. Ans. (C) | 9. Ans. (D) |
| 10. Ans. (a) $r_0 = 2a_0$, (b) 6.626×10^{-25} Å | | |
| 11. Ans. (a) 2.197×10^6 m/s (b) 3.31 Å | (c) $\sqrt{2} \cdot \frac{h}{2\pi}$ | |
| 12. Ans. (A) Q, (B) P, (C) R, (D) S | | |
| 13. Ans. (A) Q,R (B) P, Q, R,S (C) P, Q, R (D) P, Q | | |
| 14. Ans. (B) | 15. Ans. (C) | 16. Ans. (B) |
| 17. Ans. 9 | 18. Ans. 4 | 19. Ans. (C) |
| 20. Ans. (5) | 21. Ans. (6) | 22. Ans. (B) |
| 23. Ans.(B) | 24. Ans. (D) | 25. Ans. (D) |

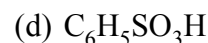
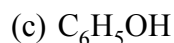
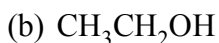
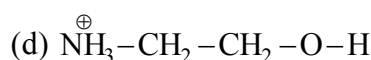
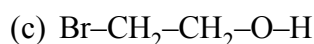
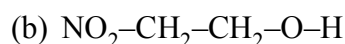
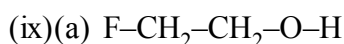
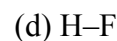
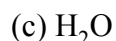
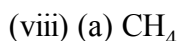
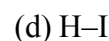
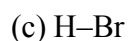
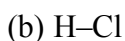
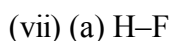
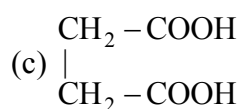
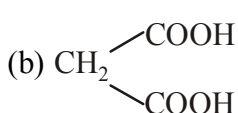
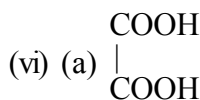
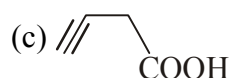
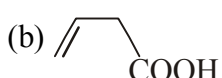
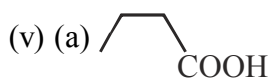
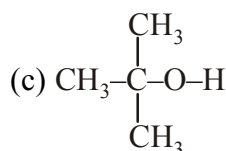
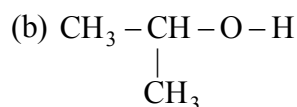
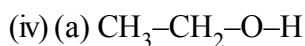
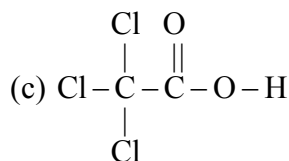
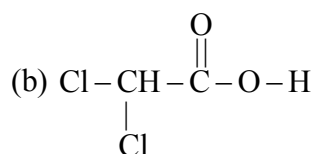
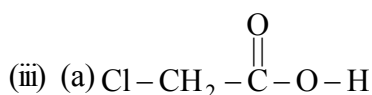
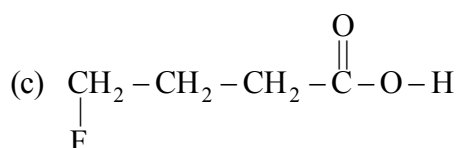
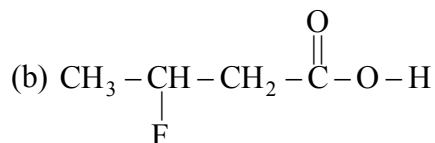
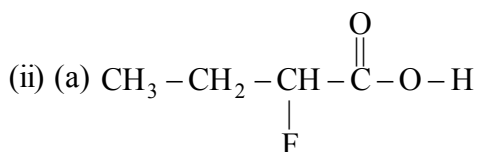
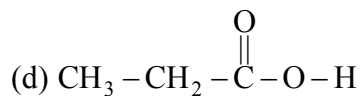
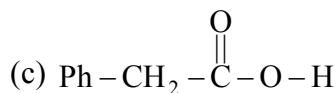
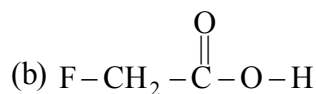
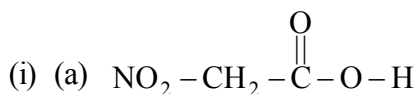
NURTURE COURSE

ACIDIC STRENGTH & BASIC STRENGTH

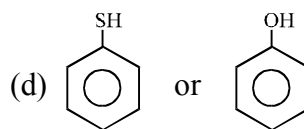
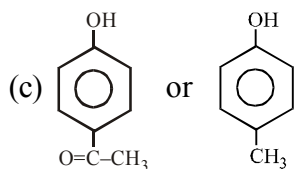
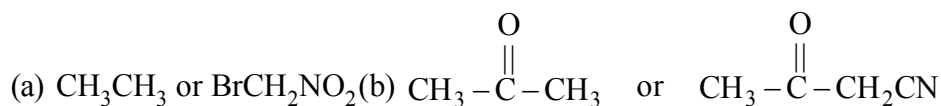
ACIDIC STRENGTH & BASIC STRENGTH

EXERCISE # I

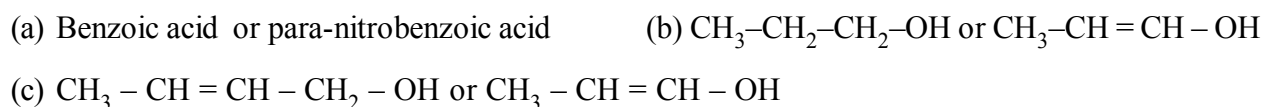
1. Write correct order of acidic strength of following compounds :



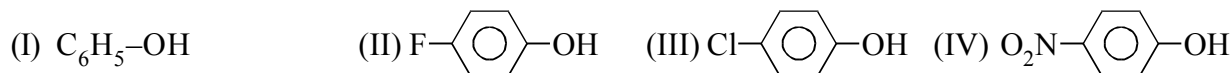
2. Explain which is a stronger acid.



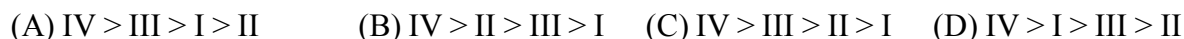
3. Which of the following would you predict to be the stronger acid ?



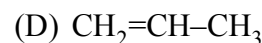
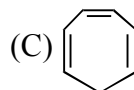
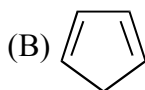
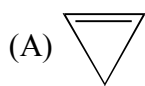
4. Arrange the given phenol & its derivative in their decreasing order of acidity :



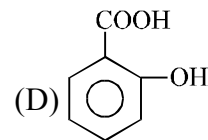
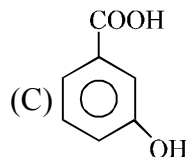
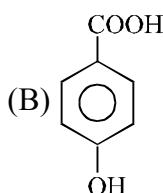
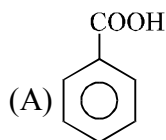
Select the correct answer from the given code:



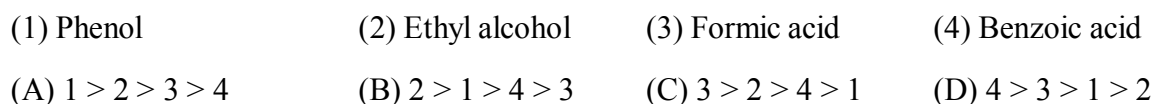
5. Which one of the following is the most acidic?



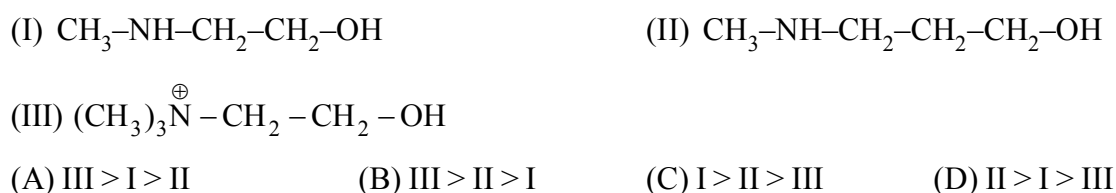
6. Which of the following is weakest acid?



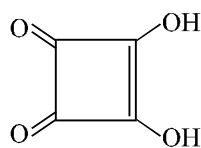
7. Arrange pH of the given compounds in decreasing order:



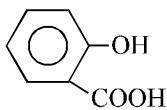
8. Arrange acidity of given compounds in decreasing order:



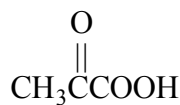
9. Consider the following compound



I



II

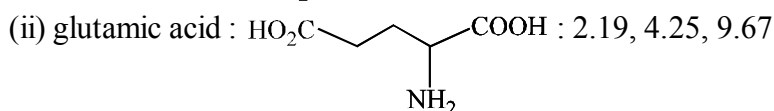
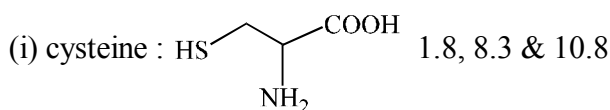


III

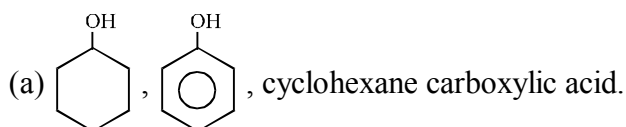
Which of the above compounds reacts with NaHCO_3 giving CO_2

- (A) I, II and III (B) I and III (C) II and III (D) I and II

10. Say which pK_a belong to which functional group in case of following amino acids :



11. Record the following sets of compounds according to increasing pK_a ($= -\log K_a$)



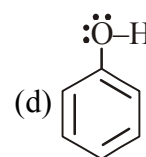
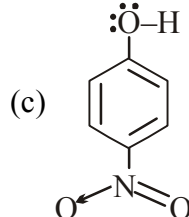
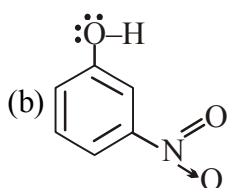
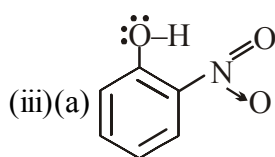
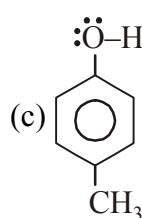
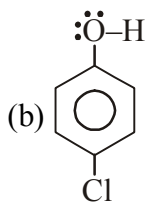
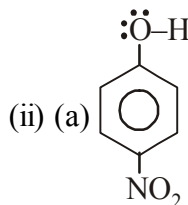
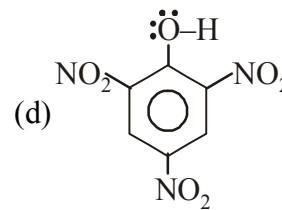
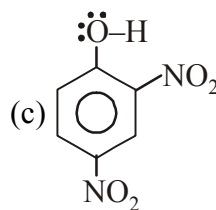
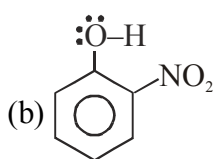
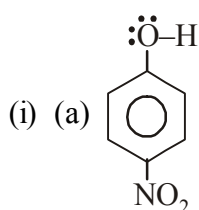
(b) 1-butyne, 1-butene, butane

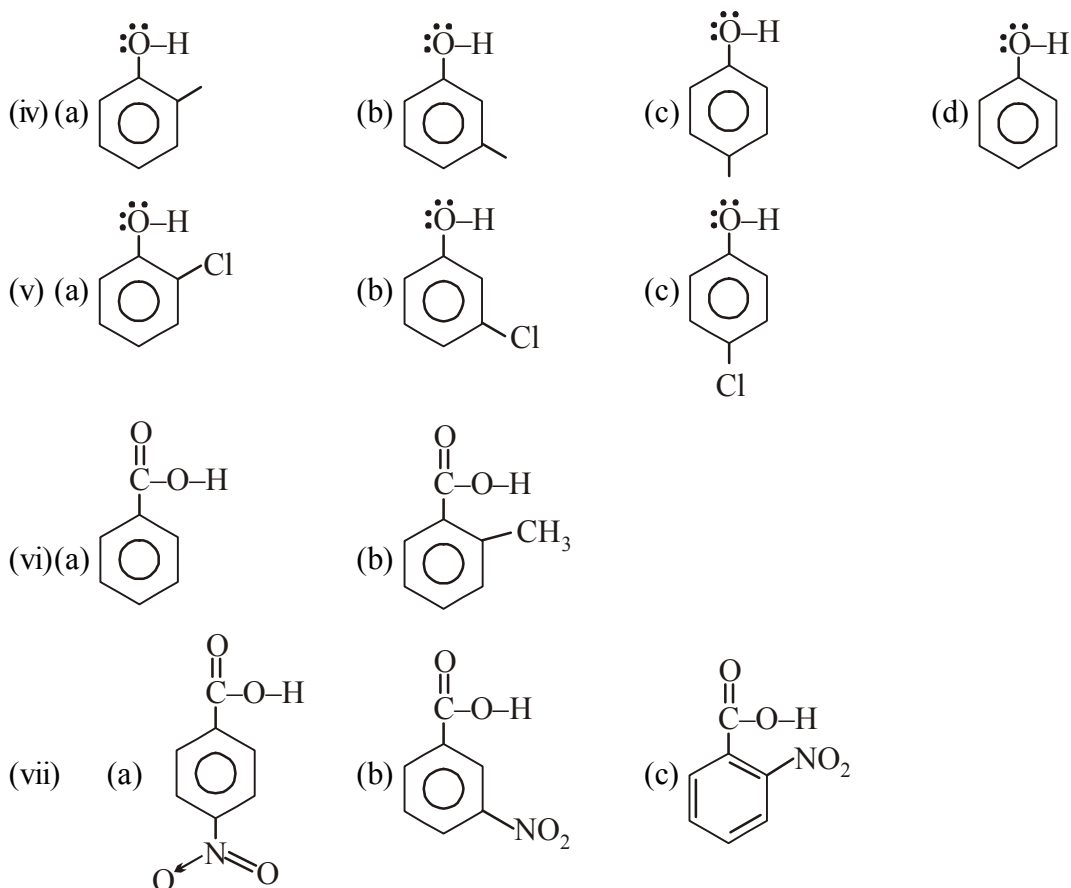
(c) Propanoic acid, 3-bromopropanoic acid, 2-nitropropanoic acid

(d) Phenol, o-nitrophenol, o-cresol

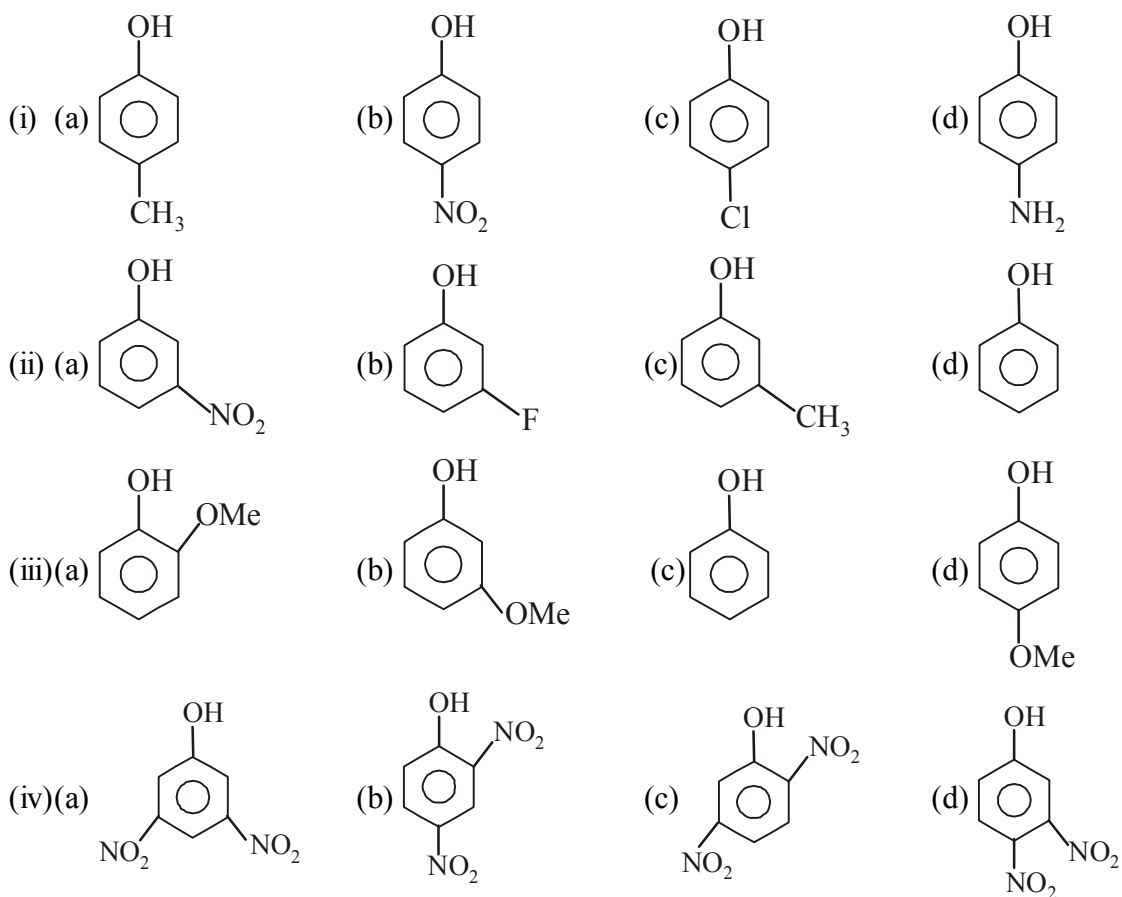
(e) Hexylamine, aniline, methylamine

12. Write correct order of acidic strength of following compounds:

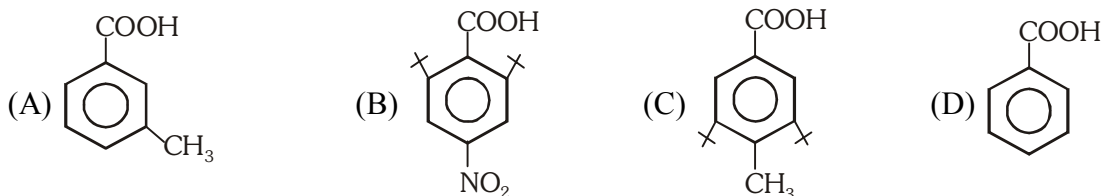




13. Select the strongest acid in each of the following sets :



14. The strongest acid is :
 (A) HF (B) $\text{CH}_3\text{CO}_2\text{H}$ (C) $\text{HF} + \text{SbF}_5$ (D) H_2S
15. The weakest acid (does not show acidic character) is :
 (A) $\text{HC} \equiv \text{CH}$ (B) $\text{CH}_2 = \text{CH}_2$ (C) Me_3CH (D) Ph_3CH
16. Which of the following is most acidic :

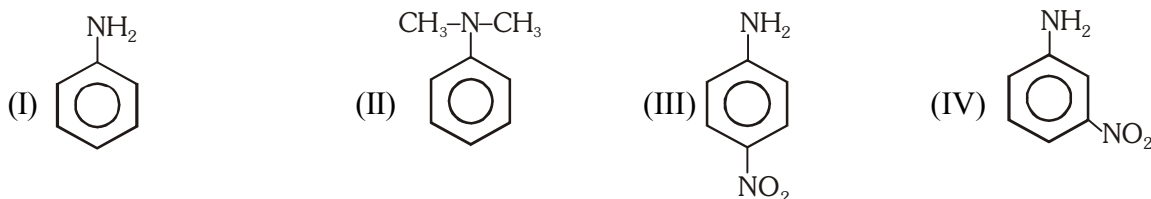


Paragraph for Question 17 to 18

The most important condition for resonance to occur is that the involved atoms in resonating structure must be coplanar or nearly coplanar for maximum delocalisation. If this condition does not fulfil, involved orbitals cannot be parallel to each other and as a consequence delocalisation cannot occur. Bulky groups present on adjacent atoms inhibit the planarity of atoms involved in resonance. This phenomenon is known as steric inhibition of resonance. Steric inhibition of resonance has profound effect on

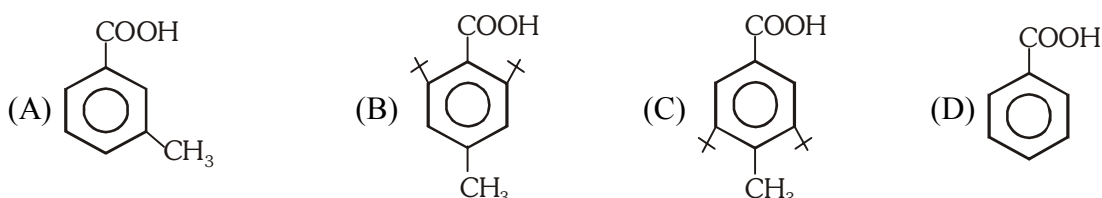
(1) Physical properties (2) Acidity and basicity (3) Reactivity of organic compounds

17. Arrange the following in the decreasing order of basicity :

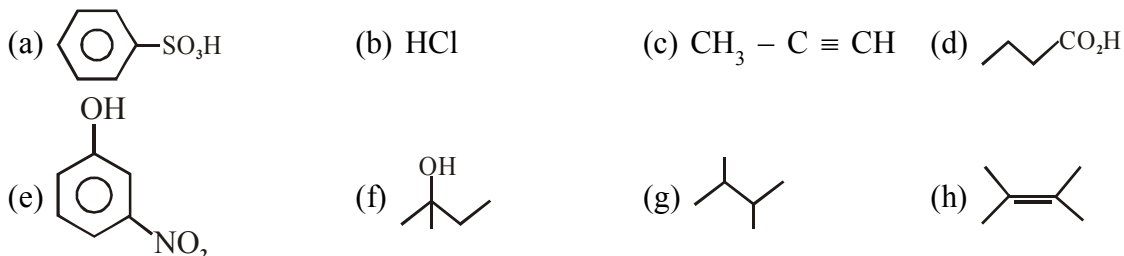


(A) $\text{I} > \text{II} > \text{III} > \text{IV}$ (B) $\text{IV} > \text{III} > \text{II} > \text{I}$ (C) $\text{II} > \text{I} > \text{IV} > \text{III}$ (D) $\text{I} > \text{IV} > \text{III} > \text{II}$

18. Which of the following is most acidic :



19. How many following compounds are more acidic than water ?



(i) NaOH

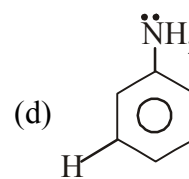
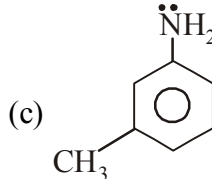
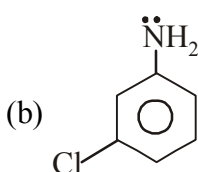
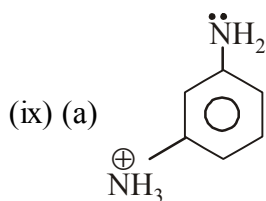
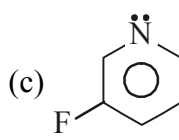
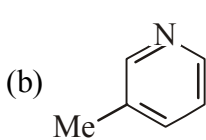
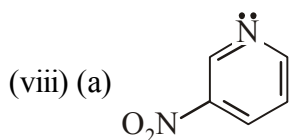
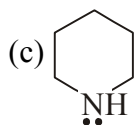
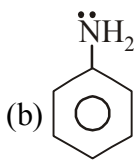
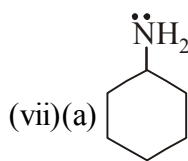
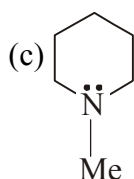
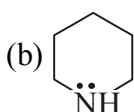
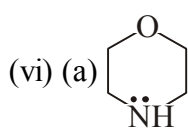
20. Select correct order regarding acidic strength of given compounds :

(1) o-methylbenzoic acid (2) m-methylbenzoic acid
 (3) p-methylbenzoic acid (4) benzoic acid
 (A) $1 > 2 > 3 > 4$ (B) $4 > 3 > 2 > 1$ (C) $1 > 4 > 2 > 3$ (D) $3 > 2 > 4 > 1$

EXERCISE # II

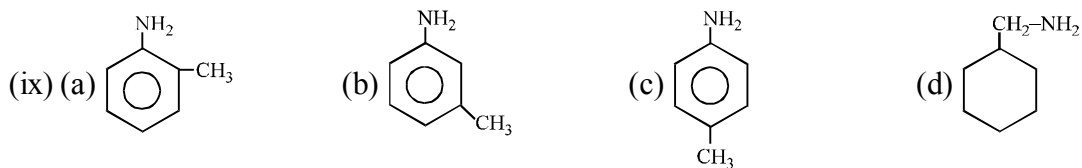
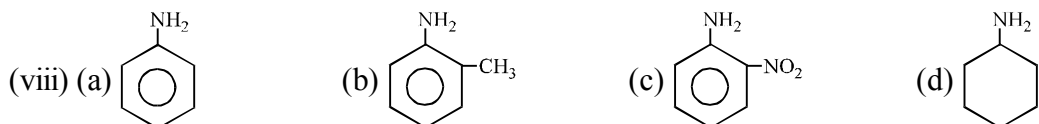
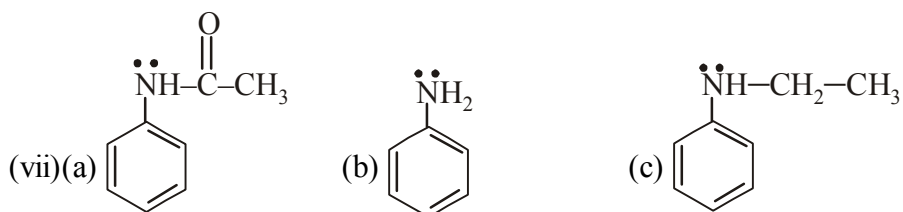
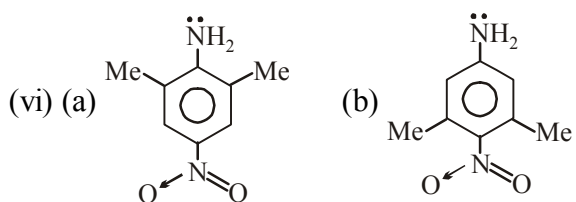
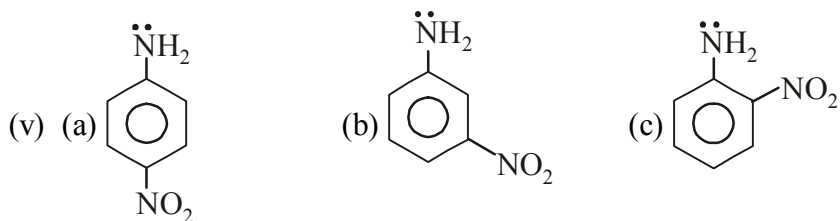
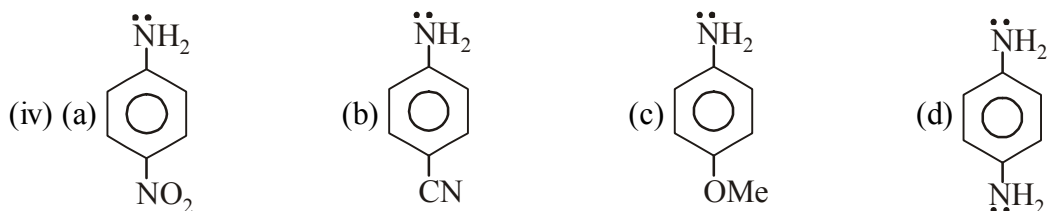
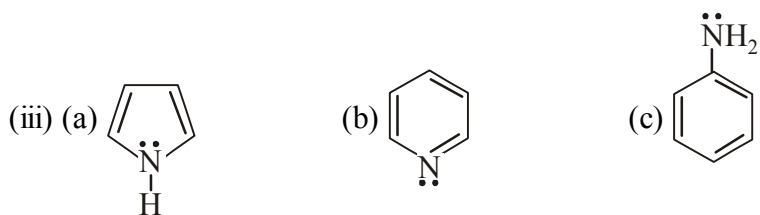
1. Write decreasing order of basic strength of following :

- (i) (a) CH_3^- (b) NH_2^- (c) OH^- (d) F^-
 (ii) (a) F^- (b) Cl^- (c) Br^- (d) I^-
 (iii) (a) NH_3 (b) MeNH_2 (c) Me_2NH (d) Me_3N (in H_2O)
 (iv) (a) NH_3 (b) MeNH_2 (c) Me_2NH (d) Me_3N (Gas phase)
 (v) (a) R-NH_2 (b) Ph-NH_2 (c) $\text{R}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{NH}_2$

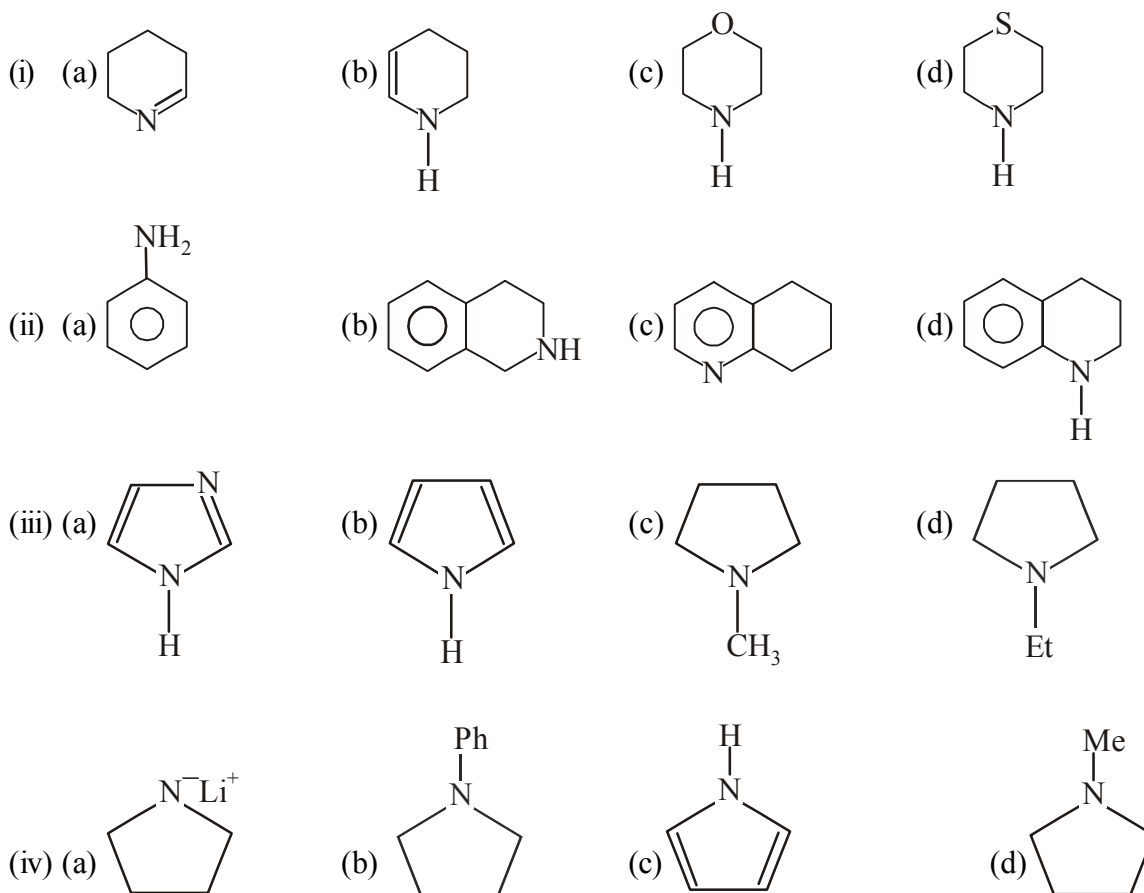


2. Write decreasing order of basic strength of following :

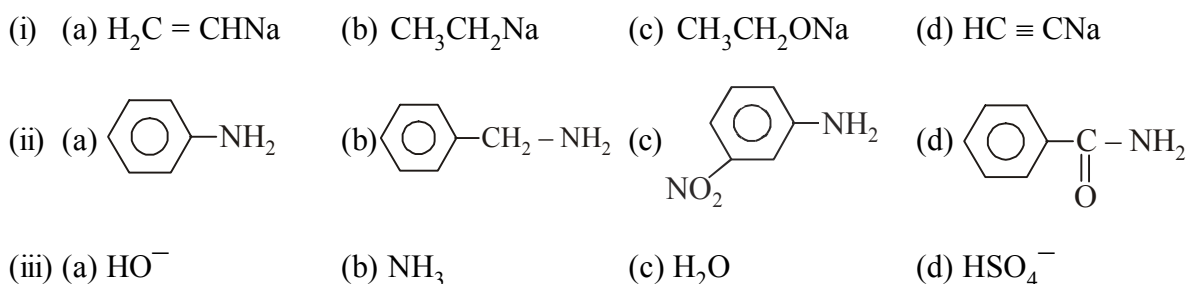
- (i) (a) $\text{CH}_3\text{-CH}_2\text{-}\ddot{\text{N}}\text{H}_2$ (b) $\text{CH}_3\text{-CH=}\ddot{\text{N}}\text{H}$ (c) $\text{CH}_3\text{-C}\equiv\ddot{\text{N}}$
 (ii) (a) $\text{CH}_3\text{-}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{-}\ddot{\text{N}}\text{H}_2$ (b) $\text{CH}_3\text{-CH}_2\text{-}\ddot{\text{N}}\text{H}_2$ (c) $\text{CH}_3\text{-}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\text{-}\ddot{\text{N}}\text{H}_2$ (d) $\ddot{\text{N}}\text{H}_2\text{-}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\text{-}\ddot{\text{N}}\text{H}_2$



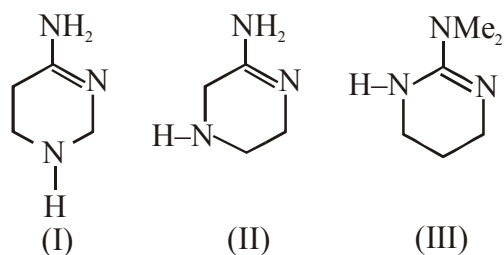
3. Select the strongest base in following compound :



4. Arrange the following compound in decreasing order of their basicity.



5. Correct decreasing order of basic strength -



Of following compound -

- (A) $\text{III} > \text{II} > \text{I}$ (B) $\text{II} > \text{I} > \text{III}$ (C) $\text{I} > \text{II} > \text{III}$ (D) $\text{III} > \text{I} > \text{II}$

6. Consider the following bases:

(I) o-nitroaniline (II) m-nitroaniline (III) p-nitroaniline

The decreasing order of basicity is:

(A) II > III > I (B) II > I > III (C) I > II > III (D) I > III > II

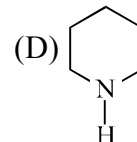
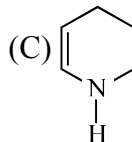
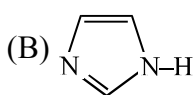
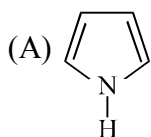
7. Consider the basicity of the following aromatic amines:

(I) aniline (II) p-nitroaniline (III) p-methoxyaniline (IV) p-methylaniline

The correct order of decreasing basicity is:

(A) III > IV > I > II (B) III > IV > II > I (C) I > II > III > IV (D) IV > III > II > I

8. Which one of the following is least basic in character?



9. In each of the following pair of compounds, which is more basic in aqueous solution?

Give an explanation for your choice:

(a) CH_3NH_2 or CF_3NH_2

(b) CH_3CONH_2 or $\text{H}_2\text{N}-\text{C}(=\text{NH})-\text{NH}_2$

(c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ or CH_3CN

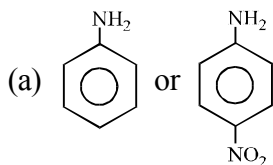
(d) $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$ or 2,6-dimethyl-N,N-dimethylaniline

10. Choose the member of each of the following pairs of compounds that is likely to be the weaker base.

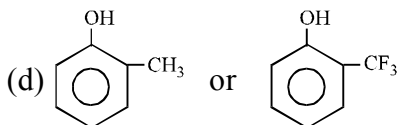
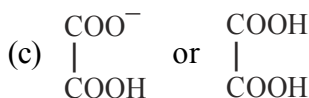
(a) H_2O or H_3O^+ (b) Cl^- , SH^- (c) F^- , OH^- , NH_2^- , CH_3^- (d) HF , H_2O , NH_3

(e) OH^- , SH^- , SeH^-

11. Explain which compound is the weaker base.

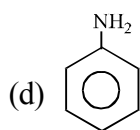


(b) $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH} - \text{CH}_2^-$ or $\text{CH}_2 = \text{CH} - \text{CH}_2^-$

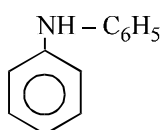


12. Arrange the basic strength of the following compounds.

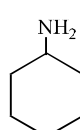
- | | | |
|--|--|--|
| (a) OH^- | CH_3COO^- | Cl^- |
| (i) | (ii) | (iii) |
| (b) $\text{CH} \equiv \text{C}^-$ | $\text{CH}_2 = \text{CH}^-$ | CH_3CH_2^- |
| (i) | (ii) | (iii) |
| (c) $\text{CH}_2 = \text{CHCH}_2\text{NH}_2$ | $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ | $\text{CH} \equiv \text{C} - \text{CH}_2\text{NH}_2$ |
| (i) | (ii) | (iii) |



(i)



(ii)

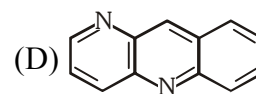
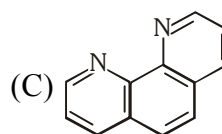
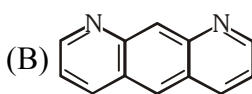
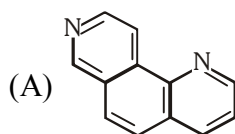


(iii)

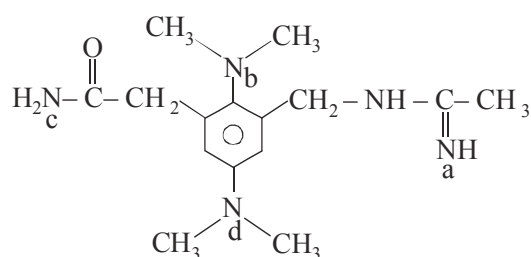
13. Arrange the following compounds in order of increasing basicity.

- (a) CH_3NH_2 , CH_3NH_3^+ , CH_3NH^- (b) CH_3O^- , CH_3NH^- , CH_3CH_2^-

14. Which of the following is most basic :

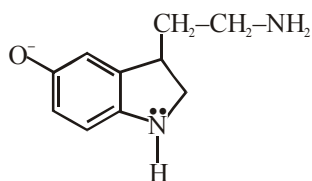


15. Basicity order of N in following compound is :



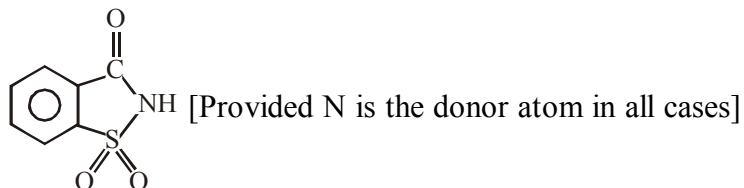
- (A) $b > d > a > c$ (B) $a > b > d > c$ (C) $a > b > c > d$ (D) $a > c > b > d$

16. The conjugate base of serotonin (used as tranquilisers) is given as follows :

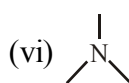
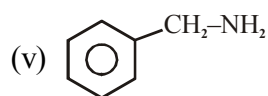
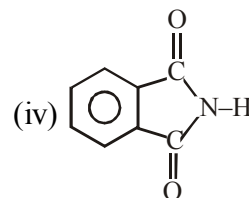
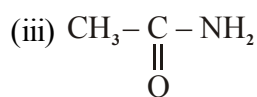
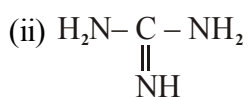
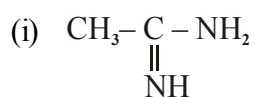


How many basic groups present in following compound ?

17. The structure of saccharin is given as follows :

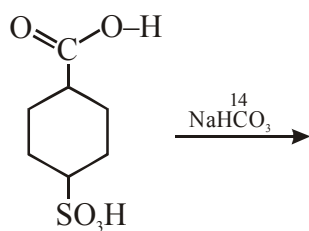


How many following compounds are more basic than saccharin ?

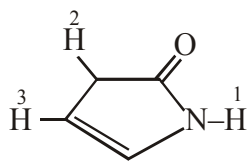


EXERCISE # III

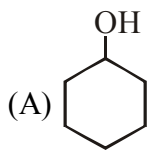
1. In given reaction Gas liberated is/are



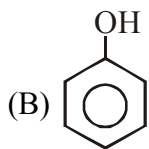
- (A) CO_2 & SO_3 (B) SO_3 & $^{14}\text{CO}_2$ (C) $^{14}\text{CO}_2$ only (D) SO_2 only
2. Arrange marked atom in decreasing order of acidic strength



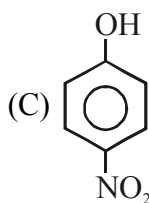
- (A) $1 > 2 > 3$ (B) $3 > 2 > 1$ (C) $2 > 1 > 3$ (D) $2 > 3 > 1$
3. **Column - I** **Column-I**



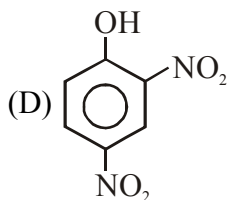
(P) React with NaOH



(Q) React with NaHCO_3



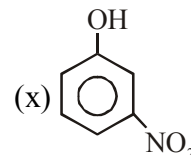
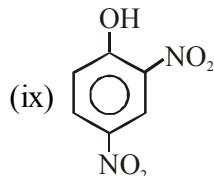
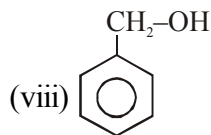
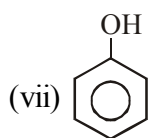
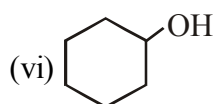
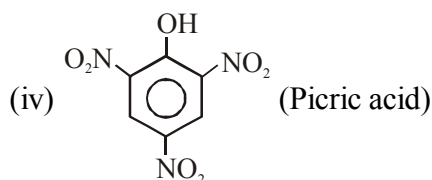
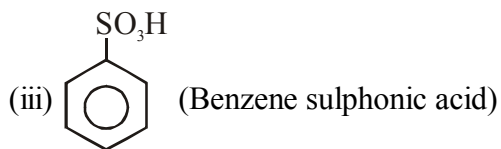
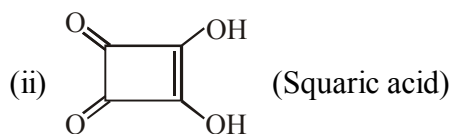
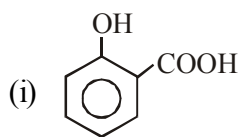
(R) React with NaH



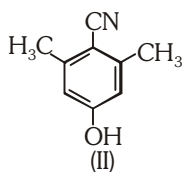
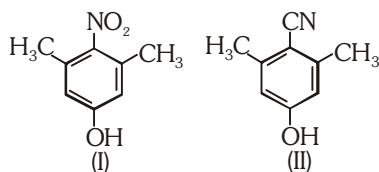
(S) React with Na

(T) React with NaNH_2

4. Compound which can give effevescences with NaHCO_3



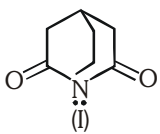
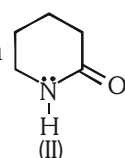
5. **Statement-1** : For the given two compounds-I is more acidic than compounds-II.



and

Statement-2 : Due to presence of $-\text{CH}_3$ group at ortho positions to $-\text{NO}_2$; the plane of $-\text{NO}_2$ deviates, w.r.t plane of ring.

- (A) Statement-1 is True, Statement-2 is True ; Statement-2 is a correct explanation for Statement-1.
 (B) Statement-1 is True, Statement-2 is True ; Statement-2 is NOT a correct explanation for Statement-1.
 (C) Statement-1 is True, Statement-2 is False.
 (D) Statement-1 is False, Statement-2 is True.

6. **Statement 1** :  (I) is more basic than  (II)

and

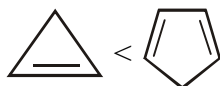
Statement 2 : Lone pair electrons on nitrogen in compound (I) does not participate in resonance.

- (A) Statement-1 is True, Statement-2 is True ; Statement-2 is a correct explanation for Statement-1.
 (B) Statement-1 is True, Statement-2 is True ; Statement-2 is NOT a correct explanation for Statement-1.
 (C) Statement-1 is True, Statement-2 is False.
 (D) Statement-1 is False, Statement-2 is True.

7. Match Column-I with Column-II.

Column - I (Facts)

- (A) Guanidine $\text{H}_2\text{N}-\text{C}(\text{NH})=\text{NH}_2$ is example of strong base
- (B) Carbanion stability $\text{CCl}_3^- > \text{CF}_3^-$
- (C) Alkyne is more acidic than alkene
- (D) Acidity :



Column - II (Reasons)

- (P) Resonance stabilisation of conjugate acid of strong base.
- (Q) Due to s-character of central atoms
- (R) Due to d-orbital resonance
- (S) Due to formation of aromatic anion
- (T) Stability of conjugate base due to more number of identical resonating structure

8. Match Column-I with Column-II.

Column - I (Compounds)

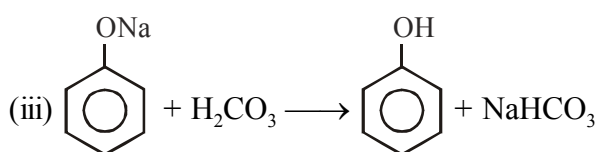
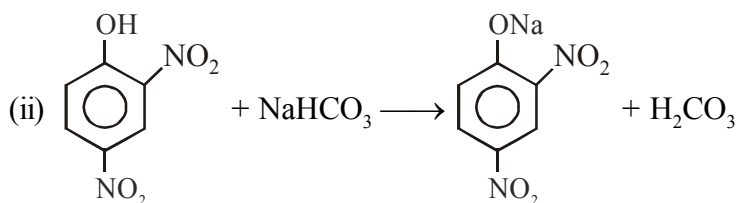
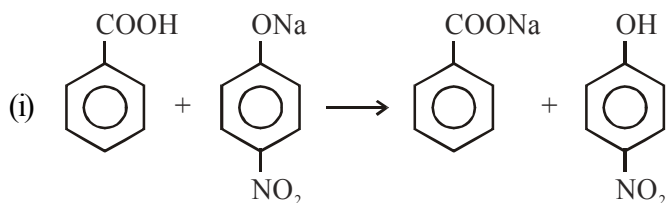
- (A)
- (B)
- (C)
- (D)

Column - II (pKa)

- (P) 7.15
- (Q) 10.14
- (R) 9.98
- (S) 9.38
- (T) pKa is more than phenol

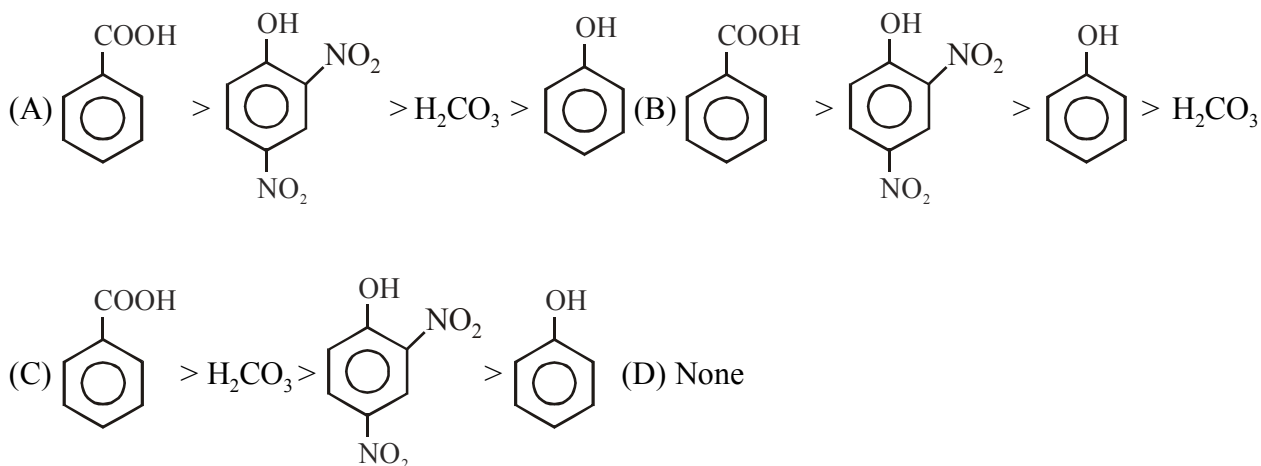
(Comprehension) (Q.9 to Q.11)

Observe the following feasible reactions :

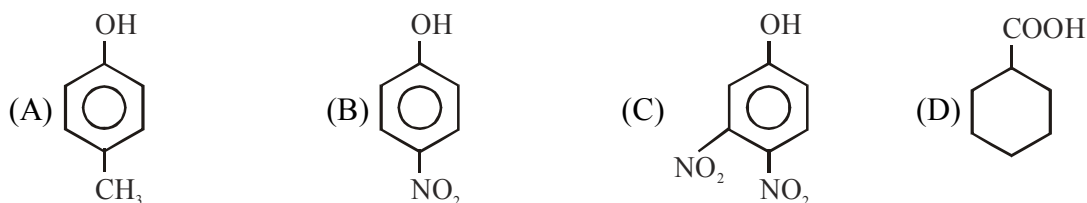


Answer the following question :

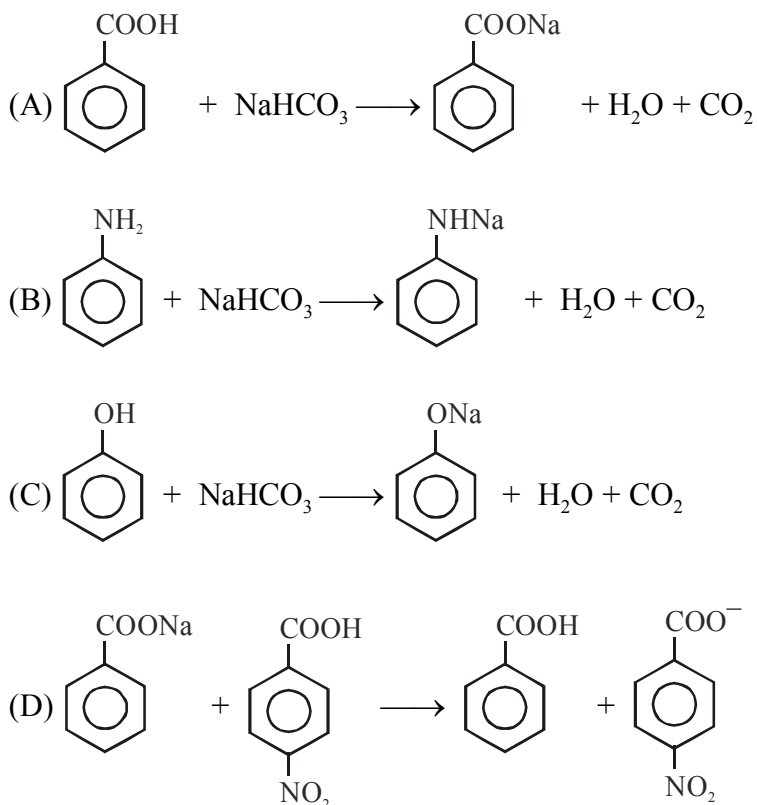
9. Which of the following is the correct order of acidic strength.



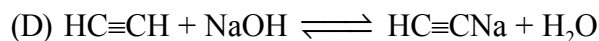
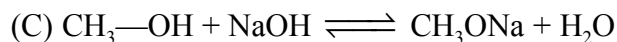
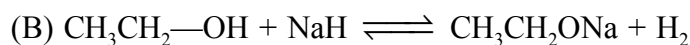
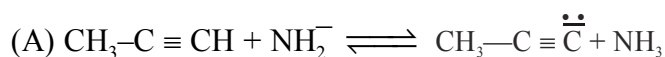
10. Which of the following compound does not react with NaHCO_3



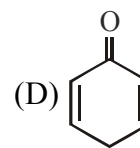
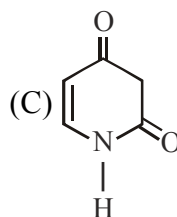
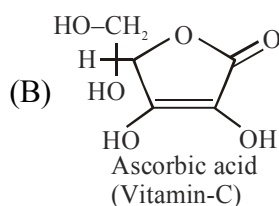
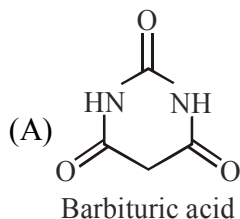
11. Identify the feasible reactions



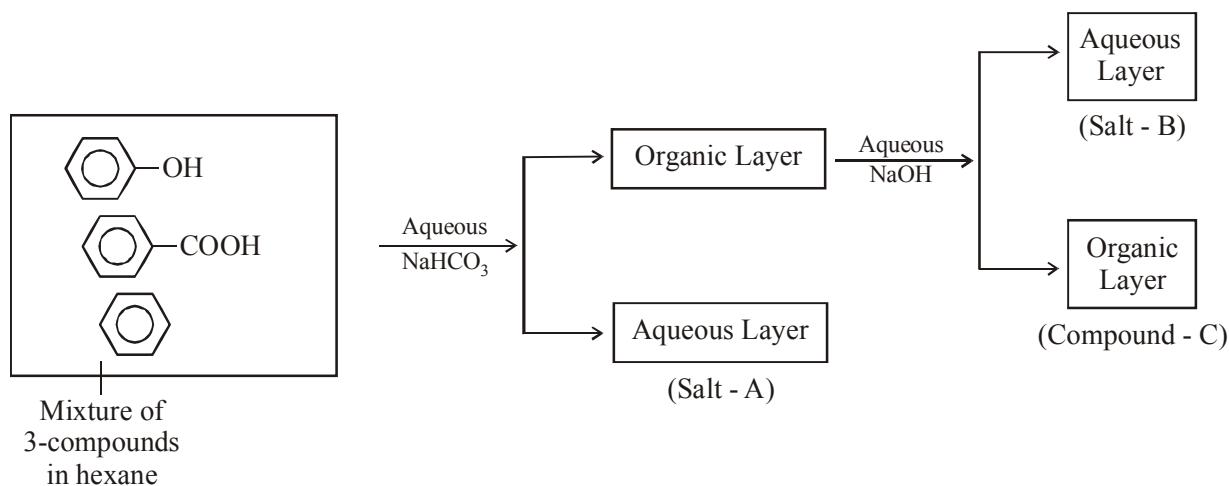
12. Identify the non-feasible reaction



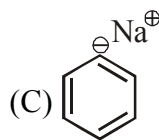
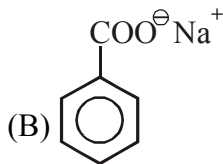
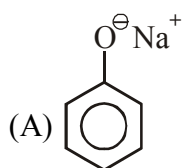
13. Select the number of compounds in which deprotonation gives aromatic anion :



Paragraph for Questions 14 and 15

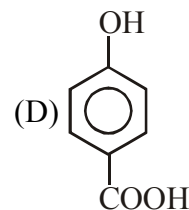
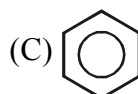
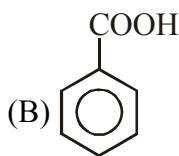
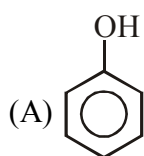


14. Identify salt 'A' ?



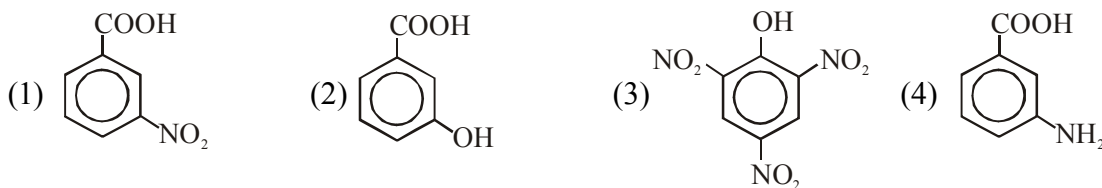
(D) All of these

15. Identify compound 'C' ?



EXERCISE # IV (JEE-MAIN)

1. Picric acid is - [AIEEE-2002]



2. Which of the following species acts both as bronsted acid & base - [AIEEE-2002]



3. The correct order of increasing basic nature for the bases NH_3 , CH_3NH_2 and $(\text{CH}_3)_2\text{NH}$ is- [AIEEE-2003]



4. Consider the acidity of the carboxylic acids- [AIEEE-2004]



which of the following is the correct order of acidity-



5. Which of the following is the strongest base - [AIEEE-2004]



6. Among the following acids which has the lowest pK_a value- [AIEEE-2005]



7. Amongst the following the most basic compound is- [AIEEE-2005]

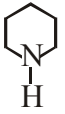

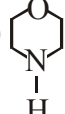



8. What is the conjugate base of OH^- ? [AIEEE-2005]



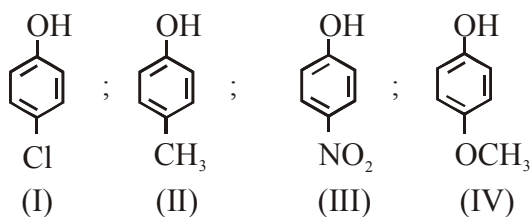
9. Among the following acids which has the lowest pK_a value? [AIEEE-2005]



10. The correct order of increasing acid strength of the compounds is [AIEEE-2006]
 (a) $\text{CH}_3\text{CO}_2\text{H}$ (b) $\text{MeOCH}_2\text{CO}_2\text{H}$
 (c) $\text{CF}_3\text{CO}_2\text{H}$ (d) $\begin{array}{c} \text{Me} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{Me} \end{array} \text{CO}_2\text{H}$
 (1) $d < a < c < b$ (2) $d < a < b < c$
 (3) $a < d < c < b$ (4) $b < d < a < c$
11. Which one of the following is the strongest base in aqueous solution ? [AIEEE-2007]
 (1) Trimethylamine (2) Aniline
 (3) Dimethylamine (4) Methylamine
12. The correct order of increasing basicity of the given conjugate base ($\text{R}=\text{CH}_3$) is :- [AIEEE-2010]
 (1) $\text{RCOO}^- < \text{HC} \equiv \text{C}^- < \text{NH}_2^- < \text{R}^-$ (2) $\text{RCOO}^- < \text{HC} \equiv \text{C}^- < \text{R}^- < \text{NH}_2^-$
 (3) $\text{R}^- < \text{HC} \equiv \text{C}^- < \text{RCOO}^- < \text{NH}_2^-$ (4) $\text{RCOO}^- < \text{NH}_2^- < \text{HC} \equiv \text{C}^- < \text{R}^-$
13. The strongest acid amongst the following compounds is ? [AIEEE-2011]
 (1) $\text{CH}_3\text{CH}_2\text{CH}(\text{Cl})\text{CO}_2\text{H}$ (2) $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{COOH}$
 (3) CH_3COOH (4) HCOOH
14. The correct order of acid strength of the following compounds :-
 A. Phenol B. p-Cresol
 C. m-Nitrophenol D. p-Nitrophenol
 is :- [AIEEE-2011]
 (1) $\text{C} > \text{B} > \text{A} > \text{D}$ (2) $\text{D} > \text{C} > \text{A} > \text{B}$
 (3) $\text{B} > \text{D} > \text{A} > \text{C}$ (4) $\text{A} > \text{B} > \text{D} > \text{C}$
15. In the following compounds : [JEE(Main)-2012]
 (I)  (II)  (III)  (IV) 
 the order of basicity is as follows :
 (1) $\text{IV} > \text{III} > \text{II} > \text{I}$ (2) $\text{II} > \text{III} > \text{I} > \text{IV}$
 (3) $\text{I} > \text{III} > \text{II} > \text{IV}$ (4) $\text{III} > \text{I} > \text{II} > \text{IV}$
16. The most basic compound among the following is :- [JEE(Main)-2012]
 (1) Acetanilide (2) Benzylamine
 (3) p-Nitro aniline (4) Aniline
17. The order of basicity of amines in gaseous state is :- [JEE(Main)-2013]
 (1) $3^\circ > 2^\circ > \text{NH}_3 > 1^\circ$ (2) $1^\circ > 2^\circ > 3^\circ > \text{NH}_3$
 (3) $\text{NH}_3 > 1^\circ > 2^\circ > 3^\circ$ (4) $3^\circ > 2^\circ > 1^\circ > \text{NH}_3$

18. Arrange the following compounds in order of decreasing acidity :

[JEE(Main)-2013]



(1) II > IV > I > III

(2) I > II > III > IV

(3) III > I > II > IV

(4) IV > III > I > II

19. The conjugate base of hydrazoic acid is :-

[JEE(Main)-2014]

(1) HN_3^-

(2) N_3^-

(3) N_2^-

(4) N^{3-}

20. Which one of the following compounds will not be soluble in sodium bicarbonate ?

[JEE(Main)-2014]

(1) Benzene sulphonic acid

(2) Benzoic acid

(3) o-Nitrophenol

(4) 2, 4, 6 - Trinitrophenol

21. Considering the basic strength of amines in aqueous solution, which one has the smallest pK_b value ?

[JEE(Main)-2014]

(1) $(\text{CH}_3)_3\text{N}$

(2) $\text{C}_6\text{H}_5\text{NH}_2$

(3) $(\text{CH}_3)_2\text{NH}$

(4) CH_3NH_2

22. Among the following oxoacids, the correct decreasing order of acid strength is : [JEE(Main)-2014]

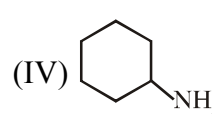
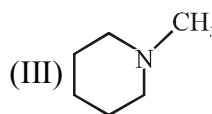
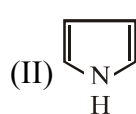
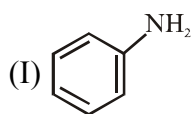
(1) $\text{HClO}_4 > \text{HClO}_3 > \text{HClO}_2 > \text{HOCl}$

(2) $\text{HClO}_2 > \text{HClO}_4 > \text{HClO}_3 > \text{HOCl}$

(3) $\text{HOCl} > \text{HClO}_2 > \text{HClO}_3 > \text{HClO}_4$

(4) $\text{HClO}_4 > \text{HOCl} > \text{HClO}_2 > \text{HClO}_3$

23. Among the following compounds, the increasing order of their basic strength is:-



(1) (II) < (I) < (III) < (IV)

(2) (I) < (II) < (IV) < (III)

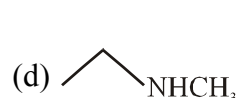
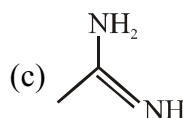
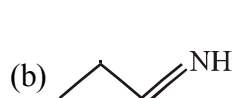
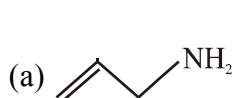
[JEE(Main)-On-Line 2017]

(3) (II) < (I) < (IV) < (III)

(4) (I) < (II) < (III) < (IV)

24. The increasing order of basicity of the following compounds is :

[JEE(Main)-2018]



(1) (b) < (a) < (c) < (d)

(2) (b) < (a) < (d) < (c)

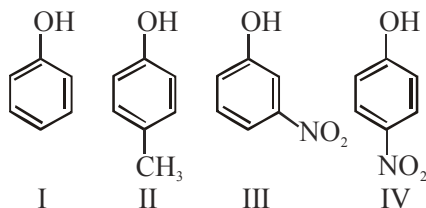
(3) (d) < (b) < (a) < (c)

(4) (a) < (b) < (c) < (d)

EXERCISE # V (J-ADVANCED)

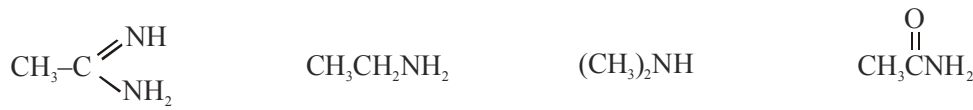
1. In the following compounds

[IIT-JEE-1996]



The order of acidity is -

- (A) III>IV>I>II (B) I>IV>III>II (C) II>I>III>IV (D) IV>III>I>II
2. Although phenoxide ion has more number of resonating structures than benzoate ion, benzoic acid is a stronger acid than phenol. Why? [IIT-JEE-1997]
3. Amongst the following, the most basic compound is - [IIT-JEE-2000]
- (A) $C_6H_5NH_2$ (B) $p\text{-NO}_2\text{-C}_6\text{H}_4\text{NH}_2$ (C) $m\text{-NO}_2\text{-C}_6\text{H}_4\text{NH}_2$ (D) $C_6H_5CH_2NH_2$
4. The correct order of basicities of the following compounds is : [IIT-JEE-2001]

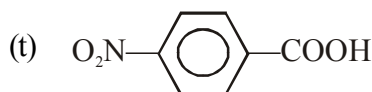
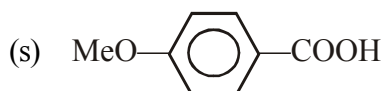
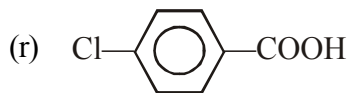
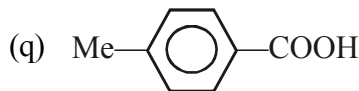
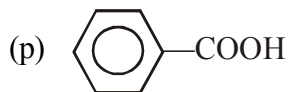


- (A) $2 > 1 > 3 > 4$ (B) $1 > 3 > 2 > 4$ (C) $3 > 1 > 2 > 4$ (D) $1 > 2 > 3 > 4$
5. **Statement-I** : p-Hydroxybenzoic acid has a lower boiling point than o-hydroxybenzoic acid.

Because**Statement-II** : o-Hydroxybenzoic acid has intramolecular hydrogen bonding. [IIT-JEE-2003]

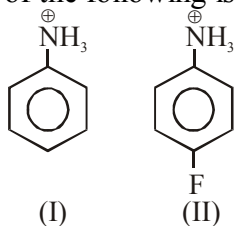
- (A) Statement-I is True, Statement-II is True ; Statement-II is a correct explanation for Statement-I
- (B) Statement-I is True, Statement-II is True; Statement-II is NOT a correct explanation for Statement-I
- (C) Statement-I is True, Statement-II is False.
- (D) Statement-I is False, Statement-II is True.
6. Match K_a values with suitable acid : [IIT-JEE-2003]

- K_a
- (A) 3.3×10^{-5}
- (B) 4.2×10^{-5}
- (C) 6.3×10^{-5}
- (D) 6.4×10^{-5}
- (E) 30.6×10^{-5}

Acid

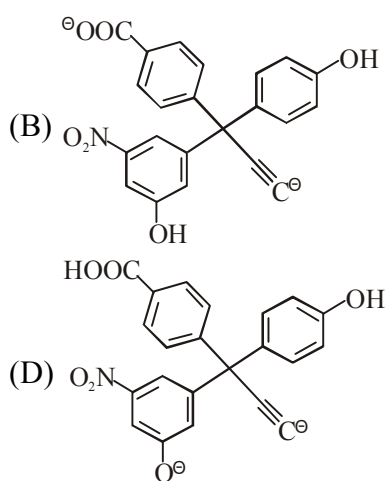
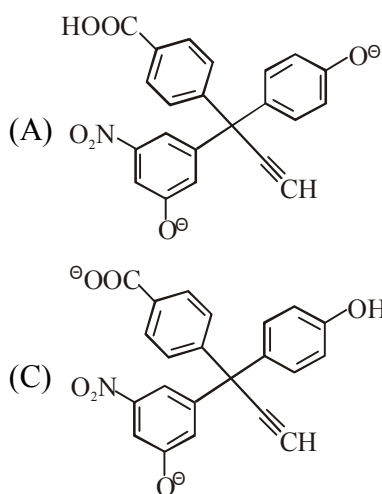
7. (a) Which of the following is more acidic and why ?

[IIT-JEE-2004]



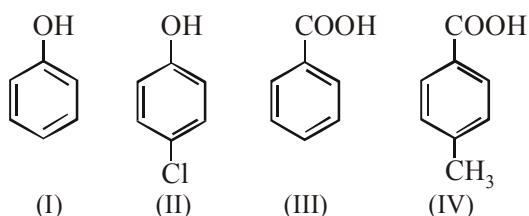
8. A. The product (A) will be :

[IIT-JEE-2007]



9. The correct acidity order of the following is :

[IIT-JEE-2009]



(A) (III) > (IV) > (II) > (I)

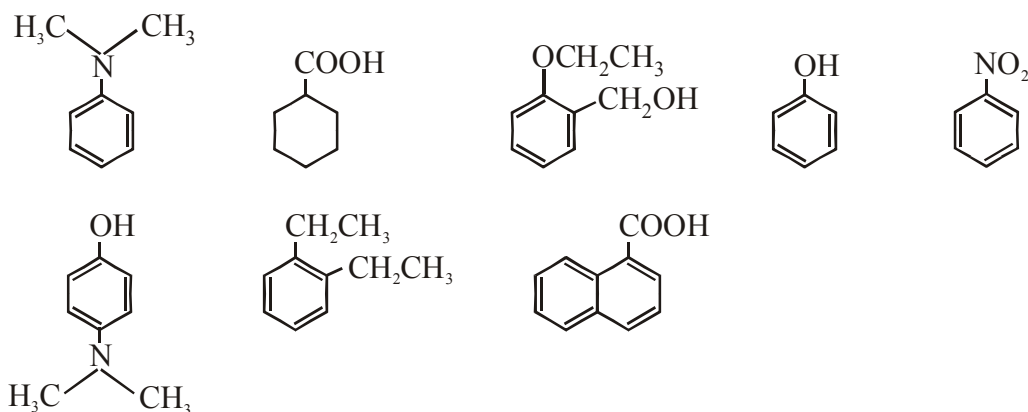
(B) (IV) > (III) > (I) > (II)

(C) (III) > (II) > (I) > (IV)

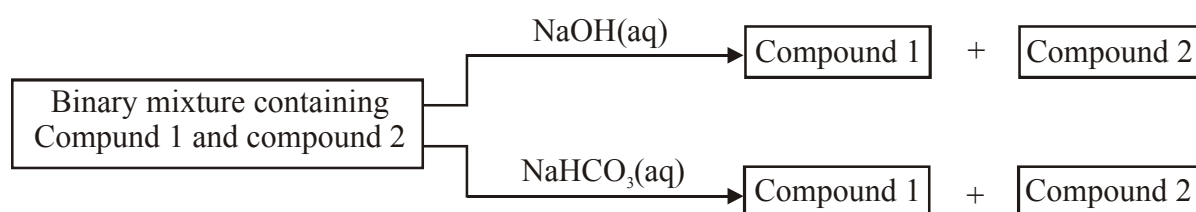
(D) (II) > (III) > (IV) > (I)

10. Amongst the following, the total number of compounds soluble in aqueous NaOH is:

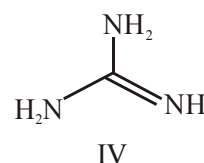
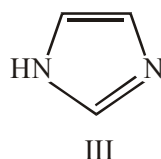
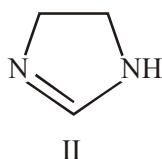
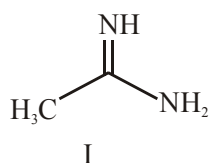
[IIT-JEE-2010]



11. Among the following compounds, the most acidic is [IIT-JEE-2011]
 (A) p-nitrophenol (B) p-hydroxybenzoic acid
 (C) o-hydroxybenzoic acid (D) p-toluic acid
12. The carboxyl functional group ($-\text{COOH}$) is present in - [IIT-JEE-2012]
 (A) picric acid (B) barbituric acid (C) ascorbic acid (D) aspirin
13. Identify the binary mixtures (s) that can be separated into the individual compounds, by differential extraction, as shown in the given scheme - [IIT-JEE-2012]



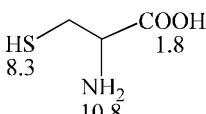
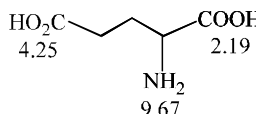
- (A) $\text{C}_6\text{H}_5\text{OH}$ and $\text{C}_6\text{H}_5\text{COOH}$ (B) $\text{C}_6\text{H}_5\text{COOH}$ and $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$
 (C) $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ and $\text{C}_6\text{H}_5\text{OH}$ (D) $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ and $\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$
14. The compound that does NOT liberate CO_2 , on treatment with aqueous sodium bicarbonate solution, is - [JEE-ADVANCED-2013]
 (A) Benzoic acid (B) Benzenesulphonic acid (C) Salicylic acid (D) Carboic acid (phenol)
15. Hydrogen bonding plays a central role in the following phenomena [JEE-ADVANCED-2014]
 (A) Ice floats in water
 (B) Higher Lewis basicity of primary amines than tertiary amines in aqueous solutions
 (C) Formic acid is more acidic than acetic acid
 (D) Dimerisation of acetic acid in benzene
16. The order of basicity among the following compounds is [JEE-ADVANCED-2017]



- (A) $\text{II} > \text{I} > \text{IV} > \text{III}$ (B) $\text{IV} > \text{II} > \text{III} > \text{I}$
 (C) $\text{I} > \text{IV} > \text{III} > \text{II}$ (D) $\text{IV} > \text{I} > \text{II} > \text{III}$

ANSWER KEY

EXERCISE # I

- $a > b > c > d$,
 - $a > b > c$,
 - $c > b > a$,
 - $a > b > c$,
 - $c > b > a$,
 - $a > b > c$
 - $d > c > b > a$,
 - $d > c > b > a$,
 - $d > b > a > c$,
 - $d > a > c > b$
- 2 ; (b) 2 ; (c) 1 ; (d) 1
- 2 ; (b) 2 ; (c) 2
- (C)
- (B)
- (B)
- (B)
- (A)
- (A)
- cysteine : 
 - glutamic acid : 
- $3 < 2 < 1$; (b) $1 < 2 < 3$; (c) $3 < 2 < 1$; (d) $2 < 1 < 3$; (e) $2 < 3 < 1$
- $d > c > a > b$,
 - $a > b > c$,
 - $c > a > b > d$,
 - $d > b > c > a$,
 - $a > b > c$,
 - $b > a$
 - $c > a > b$
- b , (ii) a , (iii) b , (iv) b
- (C)
- (C)
- (B)
- (C)
- (B)
- (4)
- (C)

EXERCISE # II

- $a > b > c > d$,
 - $a > b > c > d$,
 - $c > b > d > a$,
 - $d > c > b > a$
 - $a > b > c$,
 - $c > b > a$
 - $c > a > b$,
 - $b > c > a$,
 - $c > d > b > a$
- $a > b > c$,
 - $d > c > b > a$,
 - $b > c > a$,
 - $d > c > b > a$,
 - $b > a > c$,
 - $b > a$,
 - $c > b > a$,
 - $d > a > b > c$
 - $d > c > b > a$
- d , (ii) b , (iii) a , (iv) a
- $b > a > d > c$,
 - $b > a > c > d$,
 - $a > b > c > d$
- (A)
- (A)
- (A)
- (A)
- i , (b) ii , (c) i , (d) ii
- 2 ; (b) 1 ; (c) 2 ; (d) 2
- 1 > 2 > 3 ; (b) 1 < 2 < 3 ; (c) 3 < 1 < 2 ; (d) 2 < 1 < 3
- 2 < 1 < 3 ; (b) 1 < 2 < 3
- (C)
- (B)
- 3, 3 basic groups are $\ddot{\text{N}}\text{H}_2$; $-\text{NH}-$; O^-
- (6)

EXERCISE # III

1. (C) 2. (C)
3. (A) – R, S, T ; (B) – P, R, S, T ; (C) – P, Q, R, S, T ; (D) – P, Q, R, S, T
4. (i), (ii) (iii) (iv), (v) (ix) 5. (D) 6. (A)
7. (A) – P, T ; (B) – R ; (C) – Q ; (D) – S, T 8. (A) – R ; (B) – S ; (C) – P ; (D) – Q, T
9. (A) 10. (A) 11. (A, D) 12. (D)
13. (A, B, C, D) 14. (B) 15. (C)

EXERCISE # IV (JEE-MAIN)

- | | | | | |
|---------|---------|---------|---------|---------|
| 1. (3) | 2. (4) | 3. (3) | 4. (4) | 5. (4) |
| 6. (3) | 7. (4) | 8. (3) | 9. (1) | 10. (2) |
| 11. (3) | 12. (1) | 13. (1) | 14. (2) | 15. (3) |
| 16. (2) | 17. (4) | 18. (3) | 19. (2) | 20. (3) |
| 21. (3) | 22. (1) | 23. (3) | 24. (2) | |

EXERCISE # V (J-ADVANCED)

1. (D) 2. Benzoate has equivalent resonating structures
3. (D) 4. (B) 5. (D)
6. A-(s) ; B-(q) ; C-(p) ; D-(r) ; E-(t)
7. (II is most acidic) 8. (C) 9. (A) 10. (4)
11. (C) 12. (D) 13. (B, D) 14. (D)
15. (A, B, D) 16. (D)

NURTURE COURSE

**QUANTUM NUMBER & ELECTRONIC CONFIGURATION
PERIODIC TABLE & PERIODIC PROPERTIES
CHEMICAL BONDING**

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PERIODIC TABLE & PERIODIC PROPERTIES

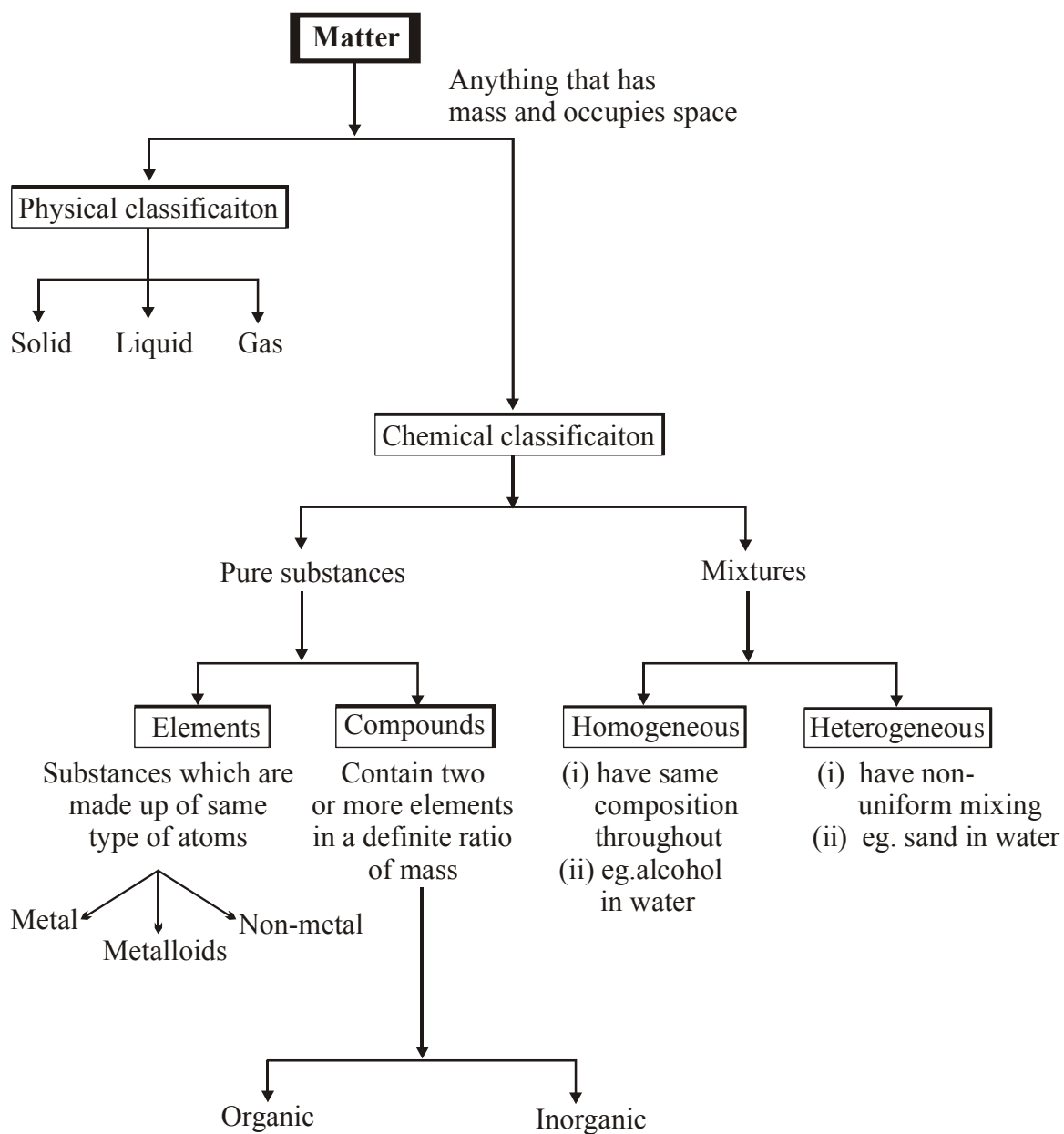
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QUANTUM NUMBER & ELECTRONIC CONFIGURATION

MATTER & ITS CLASSIFICATION



Example.1 Which of the following is homogeneous mixture :

- (A) Oil + Water (B) Milk
(C) Salt dissolved in water (D) All of these

Example.2 Which of the following molecule is tetra-atomic :

- (A) CH_2Cl_2 (B) NH_3 (C) H_2O (D) Both (B) and (C)

ATOM : An atom is the smallest particle of an element (made up of still smaller particle like electrons, protons, neutrons etc.) which can take part in a chemical reaction. It may or may not exist free in nature.

Name of particle	Mass	Nature of charge	Amount of charge	Presence in the atom
(i) Electron symbol = (e) Notation = ${}_{-1}\text{e}^0$ Discoverer J.J. Thomson (1897)	$9.11 \times 10^{-28} \text{ g}$ $\frac{1}{1837}$ th of H-atom	Negatively charged	-1.602×10^{-19} Coulomb or $-4.8 \times 10^{-10} \text{ e.s.u}$	Outside the nucleus
(ii) Proton symbol = (p) Notation = $({}_1\text{H}^1)$ Discoverer Rutherford (1911)	$1.6725 \times 10^{-24} \text{ g}$	Positively charged	$+ 1.602 \times 10^{-19}$ coulomb $+ 4.8 \times 10^{-10} \text{ e.s.u.}$	Inside the nucleus of an atom
(ii) Neutron symbol = (n) Notation = $({}_0\text{n}^1)$ Discoverer J. Chadwick (1932)	$1.675 \times 10^{-24} \text{ g}$	Neutral	0	Inside the nucleus of an atom

Representation of atom : ${}_Z^AX^A$

A → Mass number : (total number of protons + total number of neutrons present in an atom.)

Z → Atomic number : (total number of protons present in an atom.)

⇒ **Isotope** : Atoms of given element which have same atomic number but different mass number are called isotope : e.g. ${}_1\text{H}^1$, ${}_1\text{H}^2$, ${}_1\text{H}^3$ etc.

⇒ **Isobar** : Atoms of different elements with the same mass number but different atomic number .

e.g. ${}_{18}\text{Ar}^{40}$, ${}_{19}\text{K}^{40}$ and ${}_{20}\text{Ca}^{40}$

⇒ **Iso-electronic species** : Species (atom, molecules or ions) having same number of electrons are called iso-electronic e.g H^- , He, Li^+ and Be^{2+} have 2 valence electrons each.

Note : Now a days this concept is extended to consider the same valence shell electron also.

⇒ **Iso-sters** : Species having same number of electrons & same number of atoms. eg. N_2O , CO_2

⇒ **Iso-diaphers** : Species having same difference in number of neutrons and protons. eg. $^{12}_6\text{C}$, $^{16}_8\text{O}$ and $^{14}_7\text{N}$.

⇒ **Orbital** : An orbital is defined as that zone in space where electron is most likely to be found. The orbitals are characterized by a set of 3 quantum numbers (n, l, m).

QUANTUM NUMBERS : Quantum numbers give complete information about an electron or orbital in an atom.

1. Principal Quantum number (n) :

- Permissible value of **n** → 1 to ∞
- It represents shell number/energy level
- The energy states corresponding to different principal quantum numbers are denoted by letters K, L, M, N etc.

n	:	1	2	3	4	5	6
Designation of shell	:	K	L	M	N	O	P

- It indicates the distance of an electron from the nucleus.
- It also determines the energy of the electron. In general higher the value of 'n', higher is the energy of a electron.
- It give an idea of total number of orbitals & electron (which may) present in a shell & that equal to **n^2 & $2n^2$** respectively.

2. Azimuthal Quantum number (l) :

- The values of **l** depends upon the value of 'n' and possible values are '0' to (n - 1) .
- It gives the name of subshells associated with the energy level and number of subshells within an energy level.
- The different value of 'l' indicates the shape of orbitals and designated as follows :

Value	Notation	Name	Shape
$l = 0$	s	Sharp	Spherical
$l = 1$	p	Principal	Dumbell
$l = 2$	d	Diffused	Double Dumbell
$l = 3$	f	Fundamental	Complex

- It also determines the energy of orbital along with n.

For a particular energy level/shell energy of subshell is in the following order → **$s < p < d < f$**

- (v) It gives the total number of orbitals in a subshell & that equals to $(2l + 1)$ and number of electron in a subshell = $2(2l + 1)$

3. Magnetic Quantum number (m or m_l) :

- (i) The value of m depends upon the value of l and it may have integral value $-l$ to $+l$ including zero.
- (ii) It gives the number of orbitals in a given subshell and orientation of different orbitals in space.
e.g. for $n = 4$, $l = 0$ to 3 .

l	0	1	2	3
m	0	+1, 0, -1	+2, 1, 0, -1, -2	+3, +2, +1, 0, -1, -2, -3
Possible Orientation	1	3	5	7
Orbitals	s	p_x, p_y, p_z	$d_{z^2}, d_{x^2-y^2}$ d_{xy}, d_{yz}, d_{xz}	Not in syllabus

- (iii) The orbitals having same value of n and l but different value of m , have same energy in absence of external electric & magnetic field. These orbitals having same energy of a particular subshell is known as Degenerate orbitals.

4. Spin Quantum number (s) & magnetic spin quantum number (m_s) :

- (i) While moving around the nucleus, the electron always spins about its own axis either clockwise or anticlockwise. The magnetic spin quantum number represents the direction of electron spin (rotation) around its own axis (clockwise or anticlockwise).
- (ii) There are two possible values of m_s are $+\frac{1}{2}$ & $-\frac{1}{2}$ and represented by the two arrows \uparrow (spin up) and \downarrow (spin down).

RULES FOR FILLING ELECTRONS :

1. Pauli's exclusion principle

'No two electrons in an atom can have same values of all the four quantum numbers.

An orbital accommodates two electron with opposite spin. These two electrons have same values of principal, azimuthal and magnetic quantum number but the fourth, i.e. magnetic spin quantum number will be different. i.e.

For K, shell ($n = 1$)

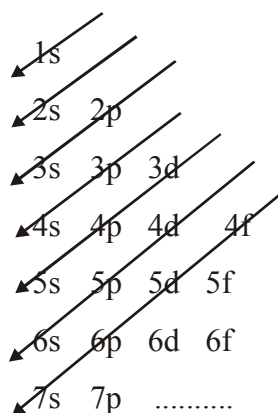
$$l = 0, m = 0$$

For 1st Electron $n = 1, l = 0, m = 0, m_s = +\frac{1}{2}$

For 2nd Electron $n = 1, l = 0, m = 0, m_s = -\frac{1}{2}$

2. Aufbau Principle (Means Building up) :

The electrons are added progressively to the various orbitals in the order of increasing energies starting with the orbital of the lowest energy



$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d < 7p$$

Alternatively, the order of increase of energy of orbitals can be calculated from $(n + l)$ rule.

- (i) Lower the value of $(n + l)$ for an orbital, the lower will be its energy.
- (ii) If two orbitals have the same $(n + l)$ value, then orbital with lower value of n has the lower energy.

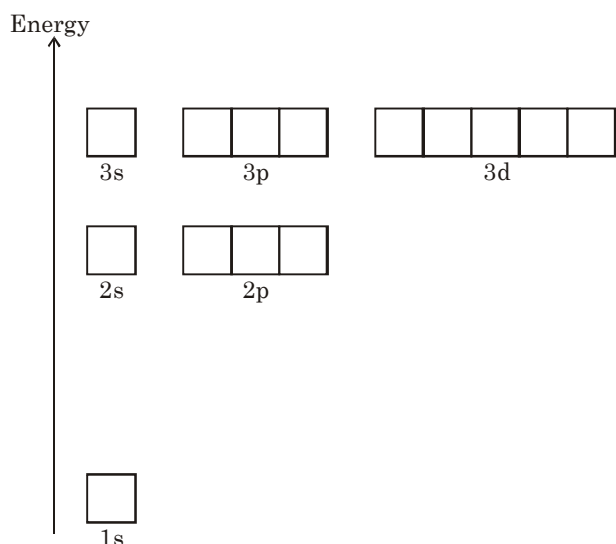
e.g. $2p$ & $3s$

For $2p$, $n = 2$, $l = 1$, $(n + l) = 2 + 1 = 3$

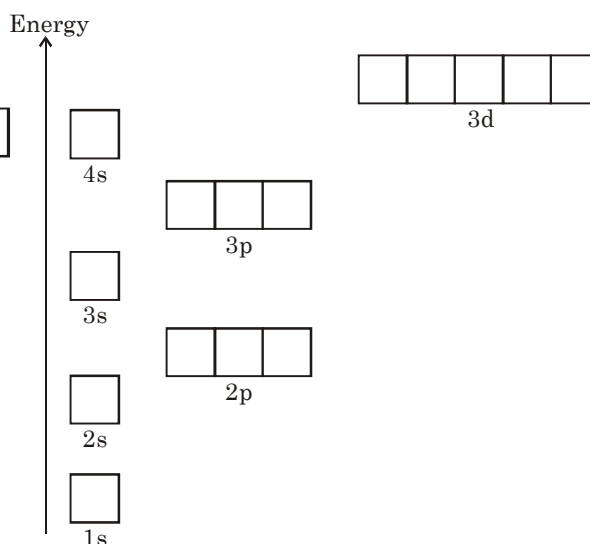
For $3s$, $n = 3$, $l = 0$, $(n + l) = 3 + 0 = 3$

Then for $2p$, n is lesser than for $3s$, so $2p$ has lower energy than $3s$.

- (iii) $1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f \dots$ energy order of different orbitals for single electron system like H, He^+ , Li^{+2} etc.



(A) For single electron or hydrogenic atom



(B) Multi electronic atoms

Energy level diagram for few electronic shells :

Example.4 Write the increasing order of energies of 4s, 3p, 4p and 3d.

Ans. For 4s, $n = 4, l = 0, (n + l) = 4$
 For 3p, $n = 3, l = 1, (n + l) = 4$
 For 4p, $n = 4, l = 1, (n + l) = 5$
 For 3d, $n = 3, l = 2, (n + l) = 5$
 $\Rightarrow 3p < 4s < 3d < 4p$ increasing order

3. **Hund's rule of maximum multiplicity :**

This rule deals with the filling of electrons into the orbitals belonging to the same subshell i.e. orbitals of equal energy, called degenerate orbitals.

“Electrons are distributed among the orbitals of a subshell in such a way as to give the maximum number of unpaired electron with parallel spins.”

“Pairing of electrons in the orbitals belonging to the same subshell (p, d, f) does not take place until each orbital belonging to that subshell has got one electron each i.e. singly occupied. Moreover, the singly occupied orbitals must have the electrons with the parallel spin multiplicity”

Multiplicity = $2|S| + 1$, where S = Total spin.



Find total spin & multiplicity

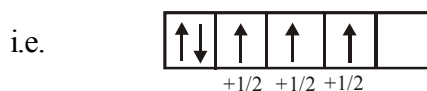
$$\text{Total spin } S = \frac{1}{2} + \frac{1}{2} + \frac{1}{2} = \frac{3}{2}$$

$$\text{Multiplicity} = 2 \times \frac{3}{2} + 1 = 4$$



$$\text{Total spin } S = \frac{1}{2} - \frac{1}{2} + \frac{1}{2} = \frac{1}{2}$$

$$\text{Multiplicity} = 2 \times \frac{1}{2} + 1 = 2$$



$$\text{Total spin } S = \frac{1}{2} + \frac{1}{2} + \frac{1}{2} = \frac{3}{2}$$

$$\text{Multiplicity} = 2 \times \frac{3}{2} + 1 = 4$$

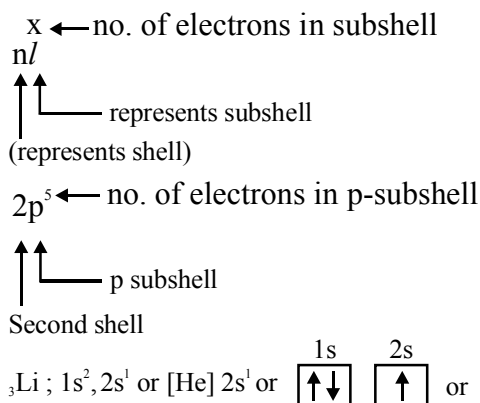


$$\text{Total spin} = 5 \times \frac{1}{2} = \frac{5}{2}$$

$$\text{Multiplicity} = 2 \times \frac{5}{2} + 1 = 6$$

ELECTRONIC CONFIGURATION OF ATOMS :

The distribution of electrons in various shells, subshells and orbitals, in an atom of an element, is called its electronic configuration.

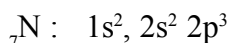


Electronic configuration :

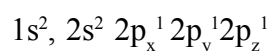
Example.5

Nitrogen

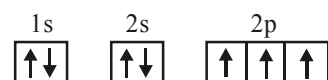
Ans.



[Orbital notation method]

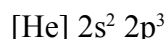


or



[Orbital diagram method]

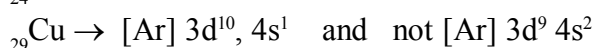
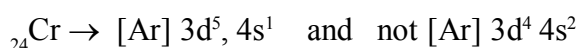
or



[Condensed form]

Extra stability of Half-filled and fully-filled orbitals.

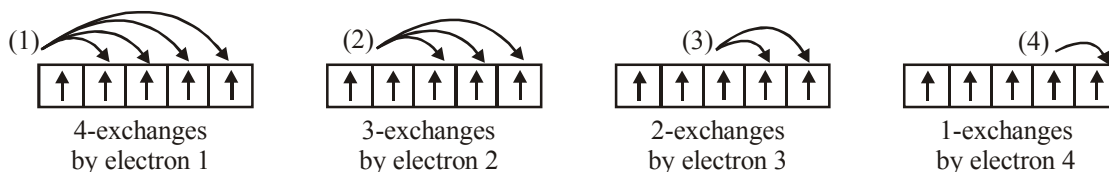
The electronic configuration of most of the atoms follows the Aufbau's rule. However, in certain elements such as Cr, Cu etc. Where the two subshells (4s and 3d) differ slightly in their energies ($4s < 3d$), an electron shifts from a subshell of lower energy (4s) to a subshell of higher energy (3d), provided such a shift results in all orbitals of the subshell of higher energy getting either completely filled or half-filled.



It has been found that there is extra stability associated with these electronic configuration. This stabilization is due to the following two factors.

- (i) **Symmetrical distribution of electron :** It is well known that symmetry leads to stability. The completely filled or half-filled subshell have symmetrical distribution of electron in them and are therefore more stable. This effect is more dominant in d and f-orbitals. This means three or six electrons in p-subshell, 5 or 10 electrons in d-subshell and 7 or 14 in f-subshell forms a stable arrangement.

- (ii) **Exchange energy** : This stabilizing effect arises whenever two or more electrons with the same spin are present in the degenerate orbitals of a subshell. These electrons tend to exchange their positions and the energy released due to this exchange is called exchange energy. The number of exchanges that can take place is maximum when the subshell is either half filled or fully filled. As a result the exchange energy is maximum and so is the stability.



Total exchange pairs = 10

$$\frac{n(n-1)}{2} \rightarrow \text{Number of exchange pairs}$$

$n \rightarrow$ Number of electron with parallel spins.

e.g. $\uparrow\downarrow \uparrow \uparrow \uparrow \uparrow$
Only 6 total exchange possible

Exceptional electronic configuration

S.No.	Element	Z	Configuration
1	Cr	24	$[\text{Ar}]4s^1 3d^5$
2.	Cu	29	$[\text{Ar}]4s^1 3d^{10}$
3.	Nb	41	$[\text{Kr}]5s^1 4d^4$
4.	Mo	42	$[\text{Kr}]5s^1 4d^5$
5.	Ru	44	$[\text{Kr}]5s^1 4d^7$
6.	Rh	45	$[\text{Kr}]5s^1 4d^7$
7.	Pd	46	$[\text{Kr}]4d^{10}$
8.	Ag	47	$[\text{Kr}]5s^1 4d^{10}$
9.	La	57	$[\text{Xe}]6s^2 5d^1$
10.	Ce	58	$[\text{Xe}]6s^2 4f^1 5d^1$
11.	Gd	64	$[\text{Xe}]6s^2 4f^7 5d^1$
12.	Pt	78	$[\text{Xe}]6s^1 4f^{14} 5d^9$
13.	Au	79	$[\text{Xe}]6s^1 4f^{14} 5d^{10}$
14.	Ac	89	$[\text{Rn}]7s^1 6d^1$
15.	Th	90	$[\text{Rn}]7s^2 6d^2$

MAGNETIC PROPERTIES :

❖ Paramagnetism :

- The substances which are weakly attracted by magnetic field are paramagnetic and this phenomenon is known as paramagnetism.
- Their magnetic character is retained till they are in magnetic field and lose their magnetism when removed from magnetic field.

❖ Diamagnetism :

- The substances which are weakly repelled by magnetic field are diamagnetic and this phenomenon is known as diamagnetism.
- Diamagnetic substances lack unpaired electrons and their spin magnetic moment is zero e.g., NaCl, N₂O₄ etc.

❖ Spin magnetic moment :

The spin magnetic moment of electron (excluding orbit magnetic moment) is given by :

$$\mu = \sqrt{n(n+2)} \text{ B.M.}$$

Where n is number of unpaired electron in species.

The magnetic moment is expressed in Bohr magneton (B.M.)

Example.6 A compound of vanadium has magnetic moment of 1.73 BM. Work out the electronic configuration of vanadium ion in the compound.

Ans. Vanadium belongs to 3d series with Z = 23. The magnetic moment of 3d series metal is given by spin only formula.

$$\mu = \sqrt{n(n+2)} \text{ BM (BM = Bohr's magneton)}$$

$$\therefore \sqrt{1.73} = \sqrt{3}$$

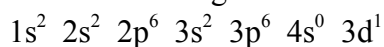
$$\Rightarrow n(n+2) = 3 \Rightarrow n = 1$$

\Rightarrow Magnetic moment correspond to one unpaired electron.

\Rightarrow Electronic configuration of vanadium atom $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$.

For one unpaired electron 4 electron must be removed in which first 2 electron are lost from 4s orbital (outermost).

Electronic configuration of V⁺⁴



Nodal Planes of different orbitals :

Nodal plane is a plane at which the probability of finding an electron becomes zero.

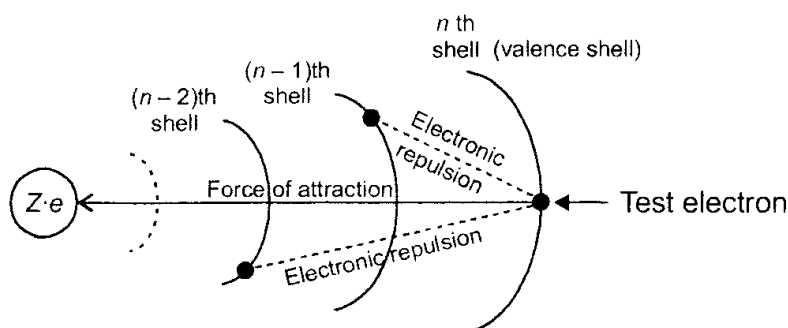
eg.

Orbital	Nodal plane	Orbital	Nodal plane
s	None	d _{xy}	XZ & YZ planes
p _x	YZ plane	d _{yz}	XZ & XY planes
p _y	XZ plane	d _{xz}	XY & YZ planes
p _z	XY plane	d _{x²-y²}	Planes perpendicular to XY plane, passing through origin (nucleus) and inclined at 45° to X & Y axis.
		d _{z²}	None (two nodal cones are available)

SCREENING EFFECT (σ) AND EFFECTIVE NUCLEAR CHARGE (Z_{eff})

- Valence shell electron suffer force of attraction due to nucleus and force of repulsion due to inner shell electrons.
- The decrease in force of attraction on valence electron due to inner shell electron is called screening effect or shielding effect. (i.e. total repulsive force is called shielding effect.)
- Due to screening effect, valence shell electron experiences less force of attraction by nucleus.
- Due to screening effect, net attractive force felt by the electron is measured by effective nuclear charge, Z_{eff}
- If nuclear charge = Z , then effective nuclear charge = $Z - \sigma$ (Where σ 'sigma' is called screening constant/shielding constant)

$$\text{So, } Z_{\text{eff}} = Z - \sigma$$

**CALCULATION OF σ (using Slater's rule)**

To calculate the shielding constant (σ) :

- Write the electronic configuration of the element in the following order and groupings :
(1s), (2s, 2p), (3s, 3p), (3d), (4s, 4p), (4d), (4f), (5s, 5p), etc.

For s and p electrons :

- Electrons in any group to the right of the (ns, np) group contribute nothing to the shielding constant.
(n-shell no. of the electron for which σ is calculated)
- All of the other electrons in the (ns, np) group, shield the concern electron to an extent of 0.35 each. (Except for the 1s orbital for which value is 0.30).
- All electrons in the (n - 1) shell shield to an extent of 0.85 each.
- All electrons (n - 2) or lower group shield completely ; that is, their contribution is 1.00 each.

For d and f electrons :

- Electrons in any group to the right of the nd or nf group contribute nothing to the shielding constant.
- All the other electrons in the nd or nf group, shield the valence electron to an extent of 0.35 each.
- All electrons in groups lying to the left of the nd or nf group contribute 1.00.

(Effective Nuclear charge of elements of second period)						
Element	Electronic Configuration	Z	σ of ns & np electron	σ (n-1) orbital	Total Screening Constant	Effective nuclear charge#
			(a)	(b)	(a + b)	$Z^* = Z - \sigma$
${}_3\text{Li}$	$1s^2 2s^1$	3	—	$0.85 \times 2 = 1.70$	1.70	1.30
${}_4\text{Be}$	$1s^2, 2s^2$	4	$1 \times 0.35 = 0.35$	$0.85 \times 2 = 1.70$	2.05	1.95
${}_5\text{B}$	$1s^2, 2s^2, 2p^1$	5	$2 \times 0.35 = 0.70$	$0.85 \times 2 = 1.70$	2.40	2.60
${}_6\text{C}$	$1s^2, 2s^2, 2p^2$	6	$3 \times 0.35 = 1.05$	$0.85 \times 2 = 1.70$	2.75	3.25
${}_7\text{N}$	$1s^2, 2s^2, 2p^3$	7	$4 \times 0.35 = 1.40$	$0.85 \times 2 = 1.70$	3.10	3.90
${}_8\text{O}$	$1s^2, 2s^2, 2p^4$	8	$5 \times 0.35 = 1.75$	$0.85 \times 2 = 1.70$	3.45	4.55
${}_9\text{F}$	$1s^2, 2s^2, 2p^5$	9	$6 \times 0.35 = 2.10$	$0.85 \times 2 = 1.70$	3.80	5.20

Calculated for valence electron.

Key Points :

- (a) From left to right in a period Z_{eff} increases
- (i) For s and p-block elements, Z_{eff} in a period increases by 0.65 where atomic number increases by 1, and hence atomic size decreases considerably.
- (ii) In transition series Z increase by + 1 but screening constant increases by 0.85 So Z_{eff} is increased by 0.15
 $(1 - 0.85 = 0.15)$ [Because e^- enters in $(n-1)$ orbit which has value of $\sigma = 0.85$]
- (b) From top to bottom in a group Z_{eff} remain constant for s-block elements, after Li and Be.

Element	Li	Na	K	Rb	Cs	Fr
Z_{eff}	1.30	2.20	2.20	2.20	2.20	2.20

Example-7 :

What is the effective nuclear charge at the periphery of nitrogen atom when an extra electron is added during the formation of an anion. Also find the value of Z_{eff} when the atom is ionized to N^+ .

Ans. Ground state electron configuration of $\text{N}(Z = 7) = 1s^2 2s^2 2p^3$

Electron configuration of $\text{N}^- = (1s^2) (2s^2 2p^4)$

Shielding constant for the last 2p electron,

$$\sigma = [(2 \times 0.85) + (5 \times 0.35)] = 3.45$$

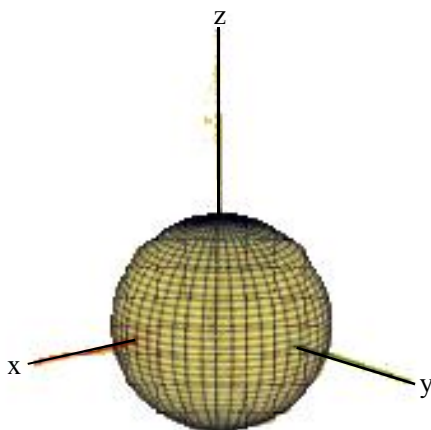
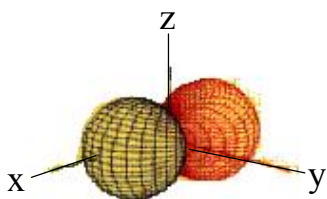
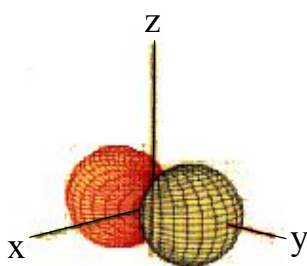
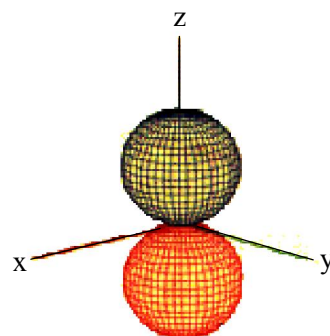
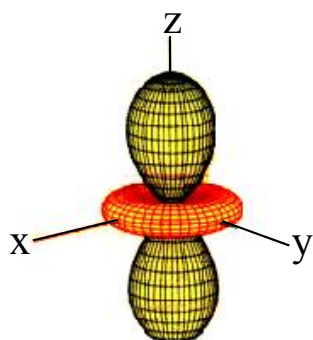
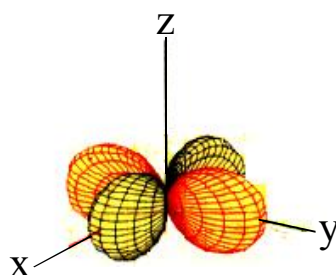
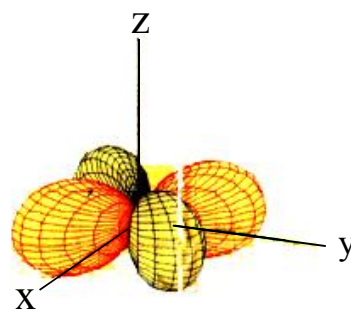
$$\text{So } Z_{\text{eff}} = Z - \sigma = 7 - 3.45 = 3.55$$

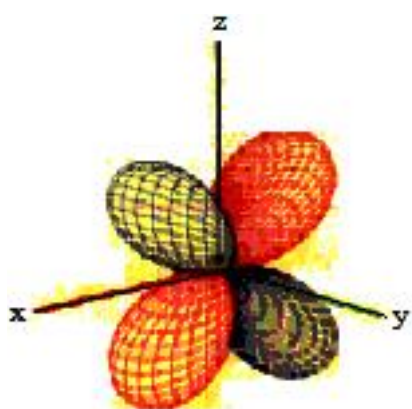
Electron configuration of $\text{N}^+ = (1s^2) (2s^2 2p^2)$

Shielding constant for the last 2p electron,

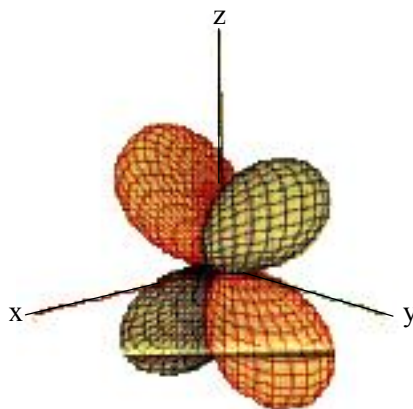
$$\sigma = [(2 \times 0.85) + (3 \times 0.35)] = 2.75$$

$$\text{So } Z_{\text{eff}} \text{ for last electron on } \text{N}^+ = 7 - 2.75 = 4.25$$

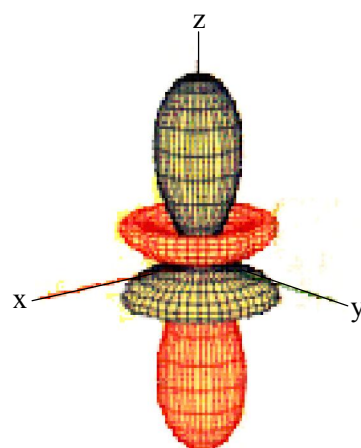
SHAPES OF ATOMIC ORBITALS**S****p_x****p_y****p_z****d_{z²}****d_{x²-y²}****d_{xy}**



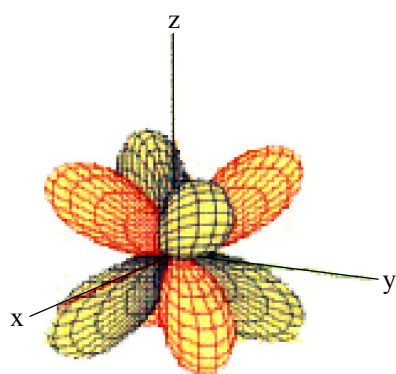
d_{xz}



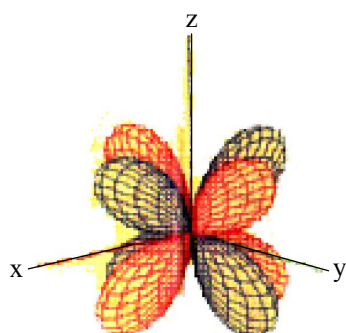
d_{yz}



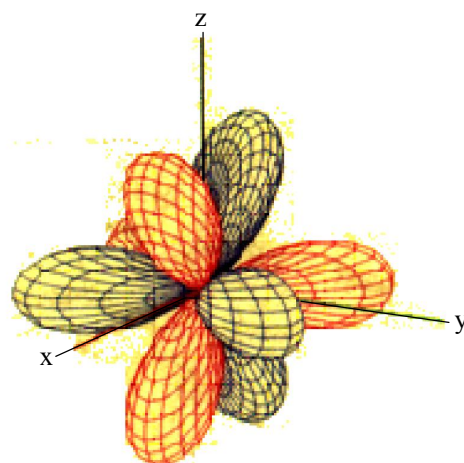
f_z^3



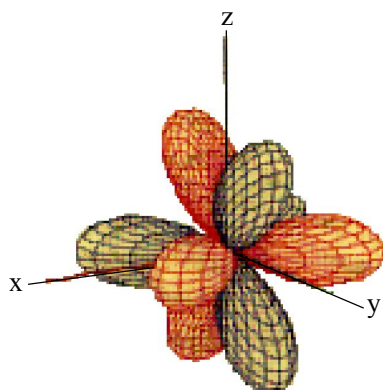
f_{xyz}



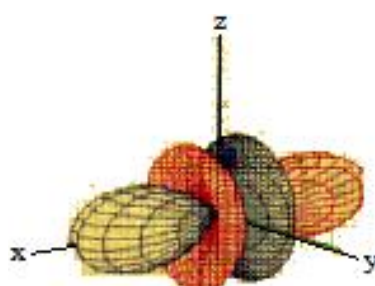
$f_{z(x^2-y^2)}$



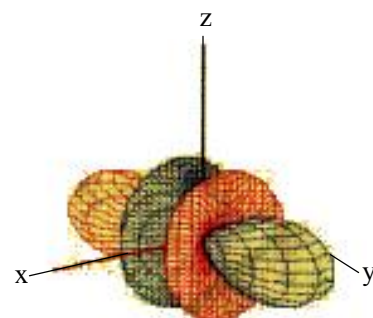
$f_{x(y^2-z^2)}$



$f_{y(z^2-x^2)}$



f_x^3



f_y^3

EXERCISE # O-1

General Introduction :

- The total number of neutrons in dipositive zinc ion with mass number 70 is
(A) 34 (B) 40 (C) 36 (D) 38
- It is known that atom contain protons, neutrons and electrons. If the mass of neutron is assumed to half of its original value where as that of proton is assumed to be twice of its original value then the atomic mass of ${}^{14}_6\text{C}$ will be -
(A) same (B) 25% more (C) 14.28 % more (D) 28.5% less
- Two monoatomic cations x^{\oplus} and y^{2+} are isoelectronic then select the correct statement : (Both elements are consecutive)
(A) Both element x and y have same number of electrons
(B) Total number of valence electrons are more in element x, than element 'y'
(C) Total number of valence electrons are more in element y, than element 'x'
(D) Both (A) and (B) are correct
- Which of the following sets contain only isoelectronic ions?
(A) Zn^{2+} , Ca^{2+} , Ga^{3+} , Al^{3+} (B) K^+ , Ca^{2+} , Sc^{3+} , Cl^-
(C) P^{3-} , S^{2-} , Cl^- , Zn^{+2} (D) Ti^{4+} , Ar , Cr^{3+} , V^{5+}

Quantum number

- Which quantum number will determine the shape of the orbital
(A) Principal quantum number (B) Azimuthal quantum number
(C) Magnetic quantum number (D) Spin quantum number
- In Palladium (Atomic no.-46), number of electron having ($\ell = 2$) will be -
(A) 20 (B) 18 (C) 16 (D) 22
- For an electron present in which of the following orbital for which ($n + l + m + s$) value is maximum. Consider maximum possible value for 'm' and minimum possible value of m_s (where ever applicable).
(A) 3p (B) 5p (C) 4d (D) 5s
- Choose the correct option for the quantum numbers of the last electron of K^+ .
(A) 4, 0, 0, $+1/2$ (B) 3, 1, -1, $-1/2$ (C) 4, 1, 0, $-\frac{1}{2}$ (D) 3, 0, 1, $\frac{1}{2}$
- Find the sum of maximum number of electrons having +1 and -1 value of 'm' in Ti (Atomic number = 22)
(A) 6 (B) 8 (C) 10 (D) 12
- The number of electrons in Ca having minimum value of $\left| \frac{n}{\ell \times m_{\ell}} \right|$ is.
(Consider only non-zero values of ℓ and m)
(A) 6 (B) 3 (C) 4 (D) None of these

Electronic Configuration

11. A neutral atom of an element has two K, eight L, nine M and two N electrons then electronic configuration of the element is
- (A) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^1$ (B) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$
 (C) $1s^2 2s^2 2p^6 3s^2 3d^2 3p^6 4s^1$ (D) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2$
12. The explanation for the presence of three unpaired electrons in the nitrogen atom can be given by
- (A) Pauli's exclusion principle (B) Hund's rule
 (C) Aufbau's principle (D) Uncertainty principle
13. If the nitrogen atom had electronic configuration $1s^7$, it would have energy lower than that of normal ground state configuration $1s^2 2s^2 2p^3$, because the electrons would be closer to the nucleus. Yet $1s^7$ is not observed because it violates :—
- (A) Uncertainty principle (B) Hund's rule
 (C) Pauli's exclusion principle (D) Bohr postulate of stationary orbits

Effective Nuclear charge (Z_{eff}) :

14. The Z_{eff} for (as Slater's rule)
- 3d electron of Cr
 4s electron of Cr
 3d electron of Cr^{3+}
 3s electron of Cr^{3+} are in the order respectively
- (A) 4.6, 2.95, 4.95, 8.05 (B) 4.95, 2.95, 4.6, 8.05
 (C) 4.6, 2.95, 5.3, 12.75 (D) none of these
15. Total number of possible shells in uranium atom (atomic no. $z = 92$)
- (A) 7 (B) 1 (C) 6 (D) None of these
16. Which of the following has the maximum number of unpaired electrons ?
- (A) Mg^{2+} (B) Ti^{3+} (C) V^{3+} (D) Fe^{2+}
17. Gaseous state electronic configuration of nitrogen atom can be represented as :
- (A) $\uparrow\downarrow \uparrow\downarrow \uparrow \uparrow \uparrow$ (B) $\uparrow\downarrow \uparrow\downarrow \uparrow \downarrow \uparrow$
 (C) $\uparrow\downarrow \uparrow\downarrow \uparrow \downarrow \downarrow$ (D) $\uparrow\downarrow \uparrow\downarrow \downarrow \downarrow \uparrow$

EXERCISE : O-2

General Introduction :

1. Isotones are :

- (A) The atoms of different elements
 (B) Have same number of neutrons
 (C) Have same number of (neutrons + protons)
 (D) Have same difference of mass number and atomic number

Quantum number

2. For an electron present in which of the following orbital for which $(n + l)$ value is maximum.

- (A) 3p (B) 5p (C) 4d (D) 5s

3. Correct set of four quantum numbers for valence electron of rubidium ($Z = 37$) is

- (A) $5, 0, 0, +\frac{1}{2}$ (B) $5, 0, 0, -\frac{1}{2}$ (C) $5, 1, 1, +\frac{1}{2}$ (D) $6, 0, 0, +\frac{1}{2}$

4. The correct set of quantum numbers for the unpaired electron of chlorine atom is

- | | n | ℓ | m | | n | ℓ | m |
|-----|----------|----------|----------|-----|----------|----------|----------|
| (A) | 2 | 1 | 0 | (B) | 2 | 1 | 1 |
| (C) | 3 | 1 | 1 | (D) | 3 | 1 | 0 |

5. Which of the following sets of quantum numbers represent an impossible arrangement ?

- | | n | ℓ | m | m_s | | n | ℓ | m | m_s |
|-----|----------|----------|----------|----------------------|-----|----------|----------|----------|----------------------|
| (A) | 3 | 3 | -2 | $\frac{1}{2}$ | (B) | 4 | 0 | 0 | $\frac{1}{2}$ |
| (C) | 3 | 2 | -3 | $\frac{1}{2}$ | (D) | 5 | 3 | 0 | $\frac{1}{2}$ |

6. The quantum numbers for the 19th electron of Cr ($Z = 24$) are

- (A) $n = 3, \ell = 0, m = 0, m_s = +\frac{1}{2}$ (B) $n = 4, \ell = 0, m = 0, m_s = +\frac{1}{2}$
 (C) $n = 3, \ell = 2, m = 2, m_s = +\frac{1}{2}$ (D) $n = 4, \ell = 0, m = 0, m_s = -\frac{1}{2}$

7. The maximum number of electron having $n \times \ell \times m = 0$ in Zn^{2+} is equal to the -

- (A) Atomic number of Mg
 (B) 12
 (C) Total number of electron in Zn which have $n + \ell = 0$
 (D) 'p' electrons in Ar

Electronic Configuration

8. The species which have same number of electrons in outer most and penultimate shell -
 (A) Ca (B) Ar (C) V^{+3} (D) Sc^{3+}
9. Which sub-shell fill completely before the 4f?
 (A) 6s (B) 5p (C) 5d (D) 4d
10. The electronic configuration of a carbon atom is $1s^2, 2s^2, 2p^2$ and consider the following four arrangements of the 2p electrons. Which arrangement have lowest energy ?
 (A)

↑↓		
----	--	--

 (B)

↑	↓	
---	---	--

 (C)

↑	↑	
---	---	--

 (D)

↑		↑
---	--	---
11. Hund's rule is applicable for :-
 (A) d-subshell (B) p-subshell (C) s-subshell (D) f-subshell
12. Which of the following has maximum number of unpaired electron.
 (A) Fe (B) Fe (II) (C) Fe (III) (D) Mn (II)
13. $Mn (Z = 25) = 1s^3 1p^9 2s^3 2p^9 2d^1$
 Which of the following change is required so that Mn have above ground state electronic configuration :
 (A) Change in the value of ℓ (azimuthal quantum number) for any subshell
 (B) Change in the possible values of ℓ (azimuthal quantum number)
 (C) Change in the Pauli rule
 (D) Change in the $(n + \ell)$ rule
14. The number of d- electrons in Mn^{2+} is equal to that of
 (A) p-electrons in N (B) s-electron in Na
 (C) d-electrons in Fe^{+3} (D) p-electrons in O^{-2}
15. Select incorrect statement(s) :
 (A) d_{z^2} orbital has different shape from rest of all d-orbitals
 (B) For the formation of cation electrons are always removed from 4s.
 (C) Zinc is a p-block element.
 (D) Principal quantum number depend upon the value of azimuthal quantum number

EXERCISE # S-1

Integer Answer Type (0 to 9) :

1. Find total no. of orbitals in nickel which have $|m| \leq 1$ and at least one electron is present, where 'm' is magnetic quantum number.

(Given your ans. as sum of digits for example. If your ans is 57 then $5 + 7 = 12$ and $1 + 2 = 3$)

2. Minimum number of electrons having $m_s = \left(-\frac{1}{2}\right)$ in Cr is “_____”.
3. How many elements are possible for the 1st period of periodic table if azimuthal quantum number can have integral values from 0 to $(n + 1)$. [n = shell number & other rules are remaining same to form periodic table.
4. Find number of unpaired electrons when Fe does not follow $(n + \ell)$ rule and filling of electron takes place shell after shell and Hund's rule is also not obeyed.
5. Find the maximum number of electrons having same Z_{eff} value for sulphur atom
6. Find the sum of maximum unpaired e^- present in one 5g & one 6g orbital.
7. Find out the maximum number of electrons that can involve in the shielding of an electron, having quantum numbers : $n = 2, \ell = 1, m = 0, m_s = +\frac{1}{2}$, in an atom.
8. Find the sum of minimum and maximum possible value of x in Fe^{+x} ion, if magnetic moment of $\text{Fe}^{+x} = 4.89$ B.M.

EXERCISE # S-2

Paragraph for Question 1 to 3

The general electronic configuration of outer most and penultimate shell is given as $(n-1)s^2 (n-1)p^6 (n-1)d^x ns^2$. Then for an element with $n = 4$ and $x = 6$.

- The number of protons present in the divalent cation of the element of above configuration is :-
(A) 24 (B) 25 (C) 26 (D) 27
- The element is :
(A) Mn (B) Fe (C) Co (D) Li
- The number of unpaired electrons in the divalent cation of the given element in isolated gaseous state is :-
(A) 0 (B) 3 (C) 4 (D) 1

Paragraph for Question 4 & 5

Consider a hypothetical atom where $p_x, p_y, p_z, d_{xy}, d_{xz}, d_{yz}$ and $d_{x^2-y^2}$ orbitals are present for principal quantum number $n = 4$.

- Find the number of other orbital which lobes are fully present in the nodal plane of p_x orbital :-
(A) 2 (B) 4 (C) 3 (D) 5
- Which of the following orbitals lobe is not present at all either in the nodal plane of p_x orbital or in the nodal plane of p_y orbital.
(A) d_{xy} (B) d_{yz} (C) $d_{x^2-y^2}$ (D) p_z

Paragraph for Question 6 & 7

Isotopes, Isobars and Iso-diaphers are some basic definitions related to the atom, which are based upon the variation in no. of electron, proton or neutrons.

- Which of the following pair represents the Isobar species :-
(A) $^{40}_{18}\text{Ar}, ^{12}_6\text{C}$ (B) $^{16}_8\text{O}, ^{14}_7\text{N}$ (C) $\text{N}_2\text{O}, \text{CO}_2$ (D) None of these
- Which of the following pair is correct for isosters :-
(A) $\text{N}_2\text{O}, \text{CH}_4$ (B) $\text{N}_2\text{O}, \text{CO}_2$ (C) CO_2, SO_2 (D) $\text{N}_2\text{O}, \text{HOCl}$

8. Column-I Element

- (P) P
(Q) N
(R) Pb
(S) Cs

Column-II

Max. value of n and ℓ respectively ; consider filled subshell only

- (1) 6, 2
(2) 3, 1
(3) 6, 3
(4) 2, 1

Code :

	P	Q	R	S
(A)	4	1	2	3
(C)	3	1	2	4

	P	Q	R	S
(B)	2	4	1	3
(D)	2	4	3	1

9. Match the following:

Column-I

- (P) Same number of unpaired electrons are present in (excluding zero)
 (Q) Same number of electrons in s & p subshells.
 (R) Same number of electrons with the $l = 1$
 (S) Same number of total electrons

Column-II

- (1) Na^+ , Mg^{2+} , F^-
 (2) F^- , Mg , O^{2-}
 (3) Mg , Ne , O^{2-}
 (4) Li , Na , K

Code :

	P	Q	R	S
(A)	1, 2	3, 4	1	4
(B)	4, 2	3, 1	2, 3	4, 1
(C)	4	1	1, 2, 3	1
(D)	3	1, 2	3, 4	1, 3, 4

10. Match the following :

Column-I (Orbital)

- (P) s
 (Q) p_x
 (R) d_{xy}
 (S) $d_{x^2-y^2}$

Column-II (Property)

- (1) Have electron density at all three axes
 (2) YZ plane is nodal plane
 (3) dumbbell shape
 (4) have azimuthal quantum no. $\ell = 2$

Code :

	P	Q	R	S
(A)	1, 3	2, 3	3	3, 4
(B)	1	2, 3	2, 4	4
(C)	1	2, 3, 4	3, 4	1, 4
(D)	2	3, 4	2, 3	1, 4

Match The Column :

11. Match the following :

Column-I (e^- configuration)

- (A) d^8
 (B) d^{10}
 (C) d^6
 (D) d^5

Column-II (Property)

- (P) Symmetrical distribution
 (Q) Unsymmetrical distribution
 (R) No of exchange pair are maximum among these
 (S) two electrons must be present in $d_{x^2-y^2}$ orbital
 (T) at least one electron is present in orbital having $m = -1$

12. **Column-I**

- (A) Zn^{2+}
 (B) Ga^+
 (C) Fe^{3+}
 (D) Br^-

Column-II

- (P) Diamagnetic
 (Q) Spin magnetic moment = $\sqrt{35}$ BM
 (R) 18 e^- in outer most shell
 (S) 3d subshell is fully filled
 (T) All the orbital of outer most shell are fully filled

MATCHING LIST TYPE 1 × 3 Q. (THREE LIST TYPE Q.)

Column - I	Column - II	Column - III
(A) Paramagnetic set	(i) $\text{Na}^+, \text{Mg}^{+2}, \text{F}^-$	(P) same value of principal quantum number for last electron
(B) Isoelectronic set	(ii) Li, Na, K	(Q) The non zero number(s) of $e^-(s)$ for $n = 3$ and $\ell \geq 1$ is
(C) The set for which value(s) of spin multiplicity is ≥ 1	(iii) $\text{Fe}^{+3}, \text{Co}^{2+}, \text{Ni}^{+2}$	(R) The value of " m_s " must be $+\frac{1}{2}$ for last electron
(D) The set of elements belongs to same period in periodic table	(iv) $\text{S}^{-2}, \text{Cl}^-, \text{P}^{-3}$	(S) Set for which the value of $m = \pm 2$ is possible for electron(s)

13. Which one of the following options is the **CORRECT** combination?
- (A) (A, i, P) (B) (B, iv, S) (C) (D, iii, S) (D) (C, iii, R)
14. Which one of the following options is the **INCORRECT** combination?
- (A) (A, iii, P) (B) (C, ii, P) (C) (B, i, P) (D) (B, iv, Q)
15. Which one of the following options is the **CORRECT** set of species with number of nodal planes for filled/partially filled orbitals is ≤ 1 for all given species in set?
- (A) (B, ii, R) (B) (B, iv, P) (C) (A, i, Q) (D) (D, iii, S)

EXERCISE # JEE-MAIN

- Which of the following groupings represent a collection of isoelectronic species ?
(At. no. Cs = 55, Br = 35) [AIEEE-2003]
(1) N^{3-} , F^- , Na^+ (2) Be , Al^{3+} , Cl^-
(3) Ca^{2+} , Cs^+ , Br (4) Na^+ , Ca^{2+} , Mg^{2+}
- The number of d-electrons retained in Fe^{2+} (At. no. of Fe = 26) ion is : [AIEEE-2003]
(1) 6 (2) 3 (3) 4 (4) 5
- Which of the following sets of quantum number is correct for an electron in 4f orbital ? [AIEEE-2004]
(1) $n = 3, \ell = 2, m = -2, s = +\frac{1}{2}$ (2) $n = 4, \ell = 4, m = -4, s = -\frac{1}{2}$
(3) $n = 4, \ell = 3, m = +1, s = +\frac{1}{2}$ (4) $n = 4, \ell = 3, m = +4, s = +\frac{1}{2}$
- Consider the ground state of Cr atom ($Z = 24$). The numbers of electrons with the azimuthal quantum numbers, $\ell = 1$ and 2 are, respectively. [AIEEE-2004]
(1) 16 and 5 (2) 12 and 5 (3) 16 and 4 (4) 12 and 4
- Which one of the following sets of ions represents the collection of isoelectronic species? [AIEEE-2004]
(1) Na^+ , Mg^{2+} , Al^{3+} , Cl^- (2) Na^+ , Ca^{2+} , Sc^{3+} , F^-
(3) K^+ , Cl^- , Mg^{2+} , Sc^{3+} (4) K^+ , Ca^{2+} , Sc^{3+} , Cl^-
- In a multi-electron atom, which of the following orbitals described by the three quantum members will have the same energy in the absence of magnetic and electric fields ? [AIEEE-2005]
(A) $n = 1, \ell = 0, m = 0$ (B) $n = 2, \ell = 0, m = 0$
(C) $n = 2, \ell = 1, m = 1$ (D) $n = 3, \ell = 2, m = 1$
(E) $n = 3, \ell = 2, m = 0$
(1) (D) and (E) (2) (C) and (D) (3) (B) and (C) (4) (A) and (B)
- Of the following sets which one does not contain isoelectronic species ? [AIEEE-2005]
(1) BO_3^{3-} , CO_3^{2-} , NO_3^- (2) SO_3^{2-} , CO_3^{2-} , NO_3^- (3) CN^- , N_2 , C_2^{2-} (4) PO_4^{3-} , SO_4^{2-} , ClO_4^-
- Which of the following statements in relation to the hydrogen atom is correct ? [AIEEE-2005]
(1) 3s, 3p and 3d orbitals all have the same energy
(2) 3s and 3p orbitals are of lower energy than 3d orbitals
(3) 3p orbital is lower in energy than 3d orbital
(4) 3s orbitals is lower in energy than 3p orbital
- Which one of the following sets of ions represents a collection of isoelectronic species ? [AIEEE-2006]
(1) N^{3-} , O^{2-} , F^- , S^{2-} (2) Li^+ , Na^+ , Mg^{+2} , Ca^{+2}
(3) K^+ , Cl^- , Ca^{+2} , Sc^{+3} (4) Ba^{+2} , Sr^{+2} , K^{+2} , Ca^{+2}
- Which of the following sets of quantum numbers represents the highest energy of an atom ? [AIEEE-2007]
(1) $n = 3, \ell = 1, m = \ell, s = +\frac{1}{2}$
(2) $n = 3, \ell = 2, m = \ell, s = +\frac{1}{2}$
(3) $n = 4, \ell = 0, m = 0, s = +\frac{1}{2}$
(4) $n = 3, \ell = 0, m = 0, s = +\frac{1}{2}$

11. Which one of the following constitutes a group of the isoelectronic species? [AIEEE-2008]
 (1) C_2^{2-}, O_2^-, CO, NO (2) $NO^+, C_2^{2-}, CN^-, N_2$
 (3) $CN^-, N_2, O_2^{2-}, C_2^{2-}$ (4) N_2, O_2^-, NO^+, CO
12. The electrons identified by quantum numbers n and ℓ :- [JEE-1999, AIEEE-2012, JEE-MAIN, (ONLINE)-2012]
 (a) $n = 4, \ell = 1$ (b) $n = 4, \ell = 0$ (c) $n = 3, \ell = 2$ (d) $n = 3, \ell = 1$
 Can be placed in order of increasing energy as
 (1) (a) < (c) < (b) < (d) (2) (c) < (d) < (b) < (a)
 (3) (d) < (b) < (c) < (a) (4) (b) < (d) < (a) < (c)
13. Which of the following paramagnetic ions would exhibit a magnetic moment (spin only) of the order of 5 BM ? [JEE-MAIN, (ONLINE)-2012]
 (At. No : Mn = 25, Cr = 24, V = 23, Ti = 22)
 (1) V^{2+} (2) Ti^{2+} (3) Mn^{2+} (4) Cr^{2+}
14. In an atom how many orbital (s) will have the quantum numbers; $n = 3, l = 2$ and $m_l = +2$? [JEE-MAIN, (ONLINE)-2013]
 (1) 1 (2) 5 (3) 3 (4) 7
15. The numbers of protons, electrons and neutrons in a molecule of heavy water are respectively [JEE-MAIN, (ONLINE)-2013]
 (1) 10, 10, 10 (2) 8, 10, 11
 (3) 10, 11, 10 (4) 11, 10, 10
16. Given [JEE-MAIN, (ONLINE)-2013]
 (a) $n=5, m_l = +1$ (b) $n = 2, l = 1, m_l = -1, m_s = -1/2$
 The maximum number of electron(s) in an atom that can have the quantum numbers as given in (a) and (b) are respectively :
 (1) 8 and 1 (2) 25 and 1 (3) 2 and 4 (4) 4 and 1
17. The correct set of four quantum numbers for the valence electrons of rubidium atom ($Z = 37$) is: [JEE(Main)-2014]
 (1) $5, 1, 1, +\frac{1}{2}$ (2) $5, 0, 1, +\frac{1}{2}$ (3) $5, 0, 0, +\frac{1}{2}$ (4) $5, 1, 0, +\frac{1}{2}$
18. If the principal quantum number $n = 6$, the correct sequence of filling of electrons will be:- [JEE-MAIN, (ONLINE)-2015]
 (1) $ns \rightarrow (n-1)d \rightarrow (n-2)f \rightarrow np$ (2) $ns \rightarrow np \rightarrow (n-1)d \rightarrow (n-2)f$
 (3) $ns \rightarrow (n-2)f \rightarrow (n-1)d \rightarrow np$ (4) $ns \rightarrow (n-2)f \rightarrow np \rightarrow (n-1)d$
19. The total number of orbitals associated with the principal quantum number 5 is : [JEE-MAIN, (ONLINE)-2016]
 (1) 25 (2) 5 (3) 20 (4) 10

EXERCISE # JEE-ADVANCED

1. The electronic configuration of an element is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$. This represents its : **[JEE 2000]**
(A) excited state (B) ground state (C) cationic form (D) none
2. The maximum number of electrons that can have principal quantum number, $n = 3$, and spin quantum number, $m_s = -1/2$, is **[JEE 2011]**
3. In an atom, the total number of electrons having quantum numbers $n=4$, $|m_\ell| = 1$ and $m_s = -\frac{1}{2}$ is: **[JEE Advanced 2014]**
4. Not considering the electronic spin the degeneracy of the second excited state ($n = 3$) of H-atom is 9, where the degeneracy of the second excited state of H^- is **[JEE Advanced 2015]**

ANSWER KEY

EXERCISE # (O-1)

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	B	C	C	B	B	A	C	B	C	C
Que.	11	12	13	14	15	16	17			
Ans.	B	B	C	C	D	D	A			

EXERCISE # (O-2)

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	A, B, D	B, C	A, B	C, D	A, C	B, D	A, B, D	B, D	A, B, D	C, D
Que.	11	12	13	14	15					
Ans.	A, B, D	C, D	B, C, D	B, C	B, C, D					

EXERCISE # (S-1)

Que.	1	2	3	4	5	6	7	8
Ans.	4	9	8	0	8	2	9	6

EXERCISE # (S-2)

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	C	B	C	C	A	D	B	D	C	B
Que.	11					12				
Ans.	(A)-Q, T (B)-P, R, S, T (C)-Q, T (D)-P, T					(A)-P, R, S, T (B)-P, S (C)-Q (D)-P, S				
Que.	13	14	15							
Ans.	C	B	B							

EXERCISE # JEE-MAIN

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	1	1	3	2	4	1	2	1	3	2
Que.	11	12	13	14	15	16	17	18	19	
Ans.	2	3	3	1	1	1	3	3	1	

EXERCISE # JEE-ADVANCED

Que.	1	2	3	4
Ans.	B	9	6	3

PART-A (PERIODIC TABLE)

INTRODUCTION :

The arrangement of all the known elements according to their properties in such a way that the elements of similar properties are grouped together in a tabular form is called periodic table.

Development of periodic table :

(A) LAVOISIER CLASSIFICATION OF ELEMENTS

At first Lavoisier classified the elements into two categories.

- (i) Metal (ii) Non-metal

Note : This classification cannot categorise the metalloid variety.

(B) DOBEREINER'S TRIAD RULE [1817]

- (i) He made groups of three elements having similar chemical properties called TRIAD.
 (ii) In Dobereiner triad, atomic weight of middle element is nearly equal to the average atomic weight of first and third element.

e.g.

Cl	Br	I	
35.5	80.0	127	$\frac{35.5 + 127}{2} = 81.25$
Ca	Sr	Ba	
40	87.5	137	$\frac{40 + 137}{2} = 88.5$
Li	Na	K	
7	23	39	At. wt of Na = $\frac{7 + 39}{2} = 23$

- (iii) Other examples – (K, Rb, Cs), (P, As, Sb), (S, Se, Te), (H, F, Cl), (Sc, Y, La)

(C) NEWLAND'S OCTAVE RULE [1865]

- (i) He arranged the elements in the increasing order of their atomic mass and observed that properties of every 8th element was similar to the 1st one, like in the case of musical vowels notation.

Sa	Re	Ga	Ma	Pa	Dha	Ni	Sa
1	2	3	4	5	6	7	8

- (ii) At that time inert gases were not known.

Li	Be	B	C	N	O	H
Na	Mg	Al	Si	P	S	F
K	Ca					Cl

- (iii) The properties of Li are similar to 8th element i.e. Na, Be are similar to Mg and so on.

Drawbacks or Limitations :

- (a) This rule is valid only upto Ca. because after Ca due to filling of d-orbitals there is difference of 18 elements instead of 8 element.
 (b) After the discovery of inert gas this law had to be dropped out.
 (c) He failed in the case of heavier metals as Fe has been placed along with O and S.

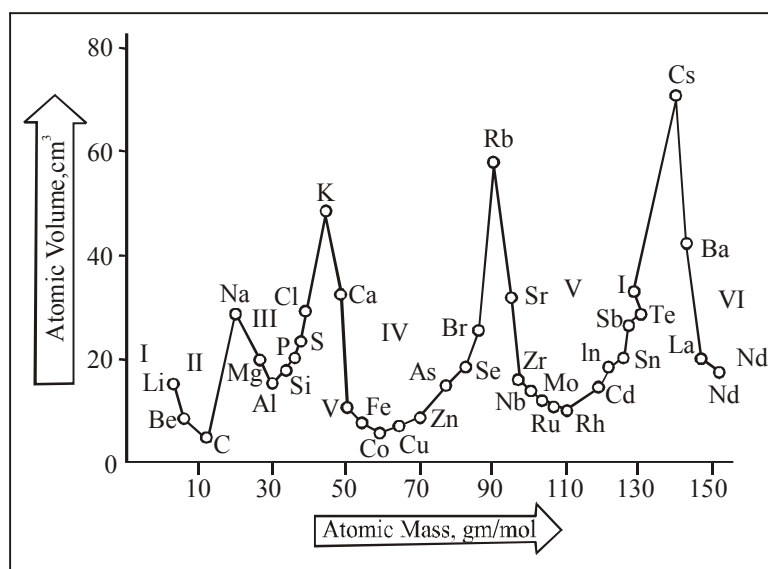
(D) LOTHER MEYER'S CURVE [1869]

- (i) He plotted a curve between atomic weight and atomic volume of different elements.
- (ii) The following observations can be made from the curve –
 - (a) Most electropositive elements i.e. alkali metals (Li, Na, K, Rb, Cs etc.) occupy the peak portions of the curve.
 - (b) Less electropositive i.e. alkaline earth metals (Be, Mg, Ca, Sr, Ba) occupy the descending portions of the curve.
 - (c) Metalloids (B, Si, As, Te, At etc.) and transition metals occupy bottom part of the curve.
 - (d) Most electronegative i.e. halogens (F, Cl, Br, I) occupy the ascending portion of the curve.

Note : Elements having similar properties occupy similar portions of the curve.

Conclusion :

On the basis of this curve, Lotther Meyer proposed that the physical properties of the elements are periodic function of their atomic weight and this became the basis of Mendeleev's periodic table.



(E) MENDELEEV'S PERIODIC TABLE [1869]

- (i) **Mendeleev's periodic law** – The physical and chemical properties of elements are the periodic function of their atomic weight
- (ii) **Characteristic of Mendeleev's periodic table** –
 - (a) It is based on atomic weight
 - (b) 63 elements were known, noble gases were not discovered.
 - (c) He was the first scientist to classify the elements in a systematic manner i.e. in horizontal rows and in vertical columns.
 - (d) Horizontal rows are called periods and there were 7 periods in Mendeleev's Periodic table.
 - (e) Vertical columns are called groups and there were 8 groups in Mendeleev's Periodic table.
 - (f) Each group upto VIIth is divided into A & B subgroups. 'A' sub group elements are called normal elements and 'B' sub group elements are called transition elements.
 - (g) The VIIIth group consists of 9 elements in three rows.
 - (h) The elements belonging to same group exhibit similar properties.

(iii) Merits or advantages of Mendeleev's periodic table –

- (a) **Study of elements** – For the first time, all known elements were classified in groups according to their similar properties. So study of the properties of elements became easier.
- (b) **Prediction of new elements** – It gave encouragement to the discovery of new elements as some gaps were left in it.

Sc (Scandium), Ga (Gallium), Ge (Germanium), Tc (Technetium) were the elements whose position and properties were well defined by Mendeleev even before their discoveries and he left the blank spaces for them in his table.

e.g. - Blank space at atomic weight 72 in silicon group was called Eka silicon (means properties like silicon) and element (*discovered later*) was named Germanium.

Similarly other elements discovered after mendeleev periodic table were :

Eka aluminium – Gallium(Ga)

Eka Boron – Scandium (Sc)

Eka Silicon – Germanium (Ge)

Eka Manganese – Technetium (Tc)

- (c) **Correction of doubtful atomic weights** – Corrections were done in atomic weight of some elements.

$$\boxed{\text{Atomic Weight} = \text{Valency} \times \text{Equivalent weight.}}$$

Initially, it was found that equivalent weight of Be is 4.5 and it is trivalent ($V = 3$), so the weight of Be was 13.5 and there is no space in Mendeleev's table for this element. So, after correction, it was found that Be is actually divalent ($V = 2$). So, the weight of Be became $2 \times 4.5 = 9$ and there was a space between Li and B for this element in Mendeleev's table.

Corrections were done in atomic weight of elements are – U, Be, In, Au, Pt.

(iv) Demerits of Mendeleev's periodic table –

- (a) **Position of hydrogen** – Hydrogen resembles both, the alkali metals (IA) and the halogens (VIIA) in properties so Mendeleev could not decide where to place it.
- (b) **Position of isotopes** – As atomic weight of isotopes differs, they should have been placed in different position in Mendeleev's periodic table. But there was no such place for isotopes in Mendeleev's table.
- (c) **Anomalous pairs of elements** – There were some pair of elements which did not follow the increasing order of atomic wts.

eg : Ar and Co were placed before K and Ni respectively in the periodic table, but having higher atomic weights.

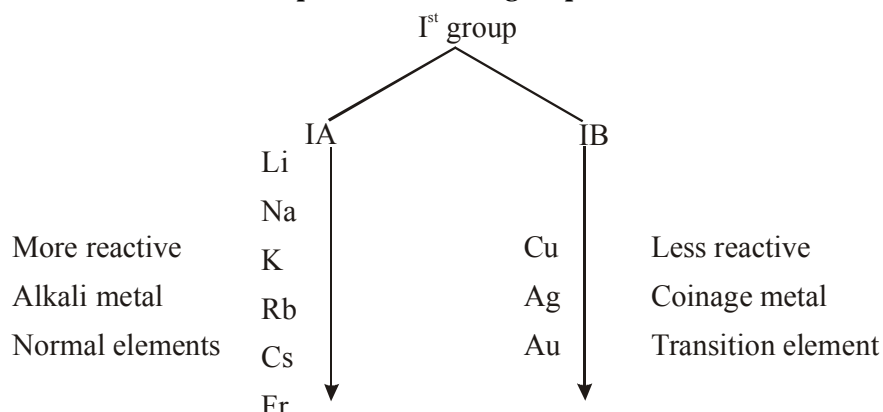
$$\begin{array}{cc} \left(\begin{array}{cc} \text{Ar} & \text{K} \\ 39.9 & 39.1 \end{array} \right) & \left(\begin{array}{cc} \text{Te} & \text{I} \\ 127.5 & 127 \end{array} \right) \\ \text{in modified mendeleev P.T.} & \\ \left(\begin{array}{cc} \text{Co} & \text{Ni} \\ 58.9 & 58.6 \end{array} \right) & \left(\begin{array}{cc} \text{Th} & \text{Pa} \\ 232 & 231 \end{array} \right) \end{array}$$

(d) Like elements were placed in different groups.

There were some elements like Platinum (Pt) and Gold (Au) which have similar properties but were placed in different groups in Mendeleev's table.

Pt	Au
VIII	IB

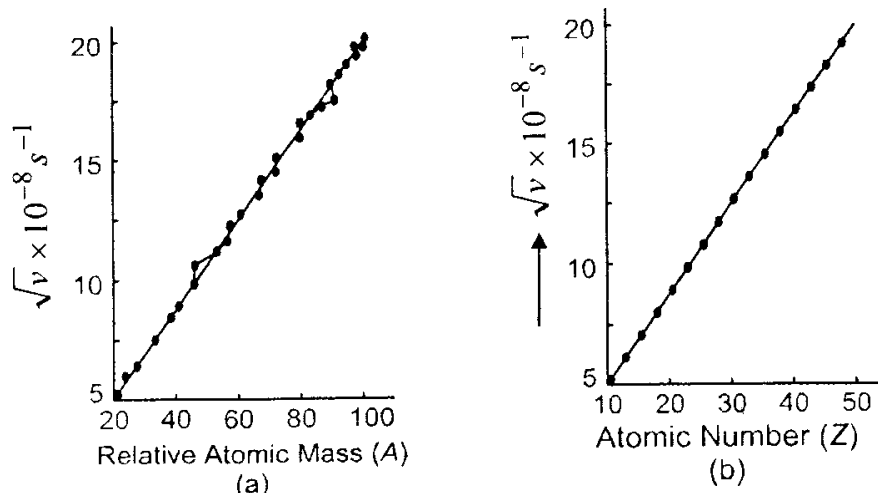
(e) Unlike elements were placed in same group.



Cu, Ag and Au placed in 1st group along with Na, K etc. While they differ in their properties (Only similar in having ns^1 electronic configuration)

(F) MODERN PERIODIC TABLE (MODIFIED MENDELEEV PERIODIC TABLE)

- (i) It was proposed by **Moseley (1913)**.
- (ii) Modern periodic table is based on atomic number.
- (iii) Moseley did an experiment in which he bombarded high speed electron on different metal surfaces and obtained X-rays.



He found out that $\sqrt{\nu} \propto Z$ (where ν = frequency) of X-rays from this experiment, Moseley concluded that the physical and chemical properties of the elements are periodic function of their atomic number. It means that when the elements are arranged in the increasing order of their atomic number, elements having similar properties gets repeated after a regular interval. This is also known as '**Modern Periodic Law**'.

- (iv) **Modern periodic law** – The physical & chemical properties of elements are a periodic function of their atomic number.
- (v) **Characteristics of modern periodic table** –
 - (a) 9 vertical columns called groups.
 - (b) IA to VIIA, IB to VIIB, VIII and 0
 - (c) Inert gases were introduced in periodic table by Ramsay.
 - (d) 7 horizontal series called periods.

(G) LONG FORM / PRESENT FORM OF MODERN PERIODIC TABLE

(It is also called as 'Bohr-Burry & Rang, Werner Periodic Table.)

- (i) It is based on the Bohr-Burry electronic configuration concept and atomic number.
 - (ii) This model was proposed by Rang & Werner
 - (iii) It consists of 7 horizontal periods and 18 vertical columns (groups)
 - (iv) According to I. U. P. A. C. 18 vertical columns are named as 1st to 18th group.
 - (v) The co-relation between the groups in long form of periodic table and in modern form of periodic table are given below.
- IA, IIA, IIIB, IVB, VB, VIB, VIIB, VIII, IB, IIB, IIIA, IVA, VA, VIA, VIIA, 0
- 1 2 3 4 5 6 7 8, 9, 10 11 12 13 14 15 16 17 18
- (vi) Elements belonging to same group have same no. of electrons in the outermost shell so their properties are similar.

Description of periods :

Period	n	Sub shell	No. of elements	Element	Name of Period
1.	1	1s	2	${}_1\text{H} - {}_2\text{He}$	Shortest
2.	2	2s, 2p	8	${}_3\text{Li} - {}_{10}\text{Ne}$	Short
3.	3	3s, 3p	8	${}_{11}\text{Na} - {}_{18}\text{Ar}$	Short
4.	4	4s, 3d, 4p	18	${}_{19}\text{K} - {}_{36}\text{Kr}$	Long
5.	5	5s, 4d, 5p	18	${}_{37}\text{Rb} - {}_{54}\text{Xe}$	Long
6.	6	6s, 4f, 5d, 6p	32	${}_{55}\text{Cs} - {}_{86}\text{Rn}$	Longest
7.	7	7s, 5f, 6d,	26	${}_{87}\text{Fr} - {}_{112}\text{Uub}$	Incomplete

CLASSIFICATION OF ELEMENTS INTO s , p , d & f-BLOCK ELEMENTS :**s – block :**

- (i) Configuration ns^{1-2}
- (ii) Last e^- enters in s orbital
- (iii) Two groups I A or 1 ; II A or 2

p – block :

- (i) Configuration $ns^2 np^{1-6}$
- (ii) Last e^- enters in p orbital
- (iii) Six groups III A , IV A , V A , VI A , VII A , zero or 13 , 14 , 15 , 16 , 17 , 18

d – block : [Transition Elements]

- (i) Configuration $(n-1)d^{1-10} ns^{0-2}$
- (ii) Last e^- enters in d orbital
- (iii) Their two outermost shell are incomplete
- (iv) 10 groups III B , IV B , V B , VI B , VII B , VIII (Triad) , I B , II B or 3 , 4 , 5 , 6 , 7 , (8 , 9 , 10) , 11 , 12 .
- (v) Four series 3d , 4d , 5d , 6d belong to 4th , 5th , 6th & 7th period respectively in long form of Periodic table.

f – block : [Inner Transition]

- (i) configuration $(n - 2) f^{0-14} (n - 1) d^{0-2} ns^2$
- (ii) last e^- enters in f orbital
- (iii) two series 4 f Lanthanides & 5 f Actinides belong to 6th & 7th period respectively in long form of Periodic table.

Neil Bohr's classification of elements :

Using electronic configuration as the criteria, elements are of four types. The classification of the elements into these groups is dependent on the extent to which the s, p, d and f orbitals are filled.

Inert Gases :

- (a) s – and p-orbitals of the outer most shell of these elements are completely filled. The outermost electronic configuration is $ns^2 np^6$.
- (b) Helium is also inert gas but its electronic configuration is $1s^2$

Representative or Normal Elements :

- (a) Outermost shell of these elements is incomplete. The number of electrons in the outermost shell is less than eight.
- (b) s-and p-block elements except inert gases are called normal or representative elements.

Transition Elements :

- (a) These metals were placed between s-block metals and p-block elements so, are named transition metals.
- (b) Their outermost electronic configuration is similar to d-block elements i.e. $(n-1) d^{1-10} ns^{1-2}$.
- (c) Last two shells of these elements namely outermost and penultimate shells are incomplete.
- (d) The last shell contains one or two electrons and the penultimate shell may contain more than eight and up to eighteen electrons.
- (e) According to definition of transition elements, those elements which have partly filled d-orbitals in neutral state or in any stable oxidation state are called transition elements. According to this definition Zn, Cd and Hg (IIB group) are d-block elements but not transition elements because these elements have d^{10} configuration in neutral as well as in stable +2 oxidation state.

Inner Transition Elements :

- (a) In these elements last three shells i.e. last, penultimate and prepenultimate shells are incomplete.
- (b) These are related to IIIB i.e. group 3.
- (c) The last shell contains two electrons. Penultimate shell may contain eight or nine electrons and pre-penultimate shell contains more than 18, up to 32 electrons.
- (d) Their outermost electronic configuration is similar to f-block element
i.e. $(n - 2) f^{0-14} (n - 1) d^{0-2} ns^2$

METALS, NON-METALS & METALLOIDS

Apart from classifying elements into s, p, d and f-blocks, there is yet another broad classification of elements based on their properties. The elements can be broadly classified into

(a) Metals:

Majority of the elements in periodic table are metals and appears on the left side of the periodic table.

Properties:

- (i) These are usually solid at room temperature [exception - mercury]
- (ii) They have high melting and boiling point [exception Gallium & Cesium have very low melting point (303 K and 302 K respectively)]
- (iii) They are good conductor of heat and electricity.
- (iv) They are malleable (can be flattened into thin sheets by hammering) and ductile (can be drawn into wires)

(b) Non-Metals:

These are placed at the top right hand side of periodic table. As we move horizontally along a period, the property of elements changes from metallic (on left) to non-metallic (on the right).

Properties :


- (i) These are usually solids or gases at room temperature.
- (ii) They have low melting point and boiling point (exception : Boron, Carbon).
- (iii) Most Non-metallic solids are brittle and are neither malleable nor ductile.

(c) Metalloids (Semi-metals):

Properties of these elements show the characteristics of both metals and non-metals. Silicon (Si), Germanium(Ge), Arsenic(As), Antimony(Sb) and Tellurium(Te) are metalloids.

ESTIMATING POSITION OF AN ELEMENT FROM ITS ELECTRONIC CONFIGURATION

The last electron enters in which subshell gives idea of its block.

 **Think** : $1s^1$ and $1s^2$ belongs to which block]

Period number = Principal quantum number of valence shell electron in ground state electronic configuration.

Group number for s block = number of valence shell electrons

Group number for p block = 10 + number of valence shell electrons

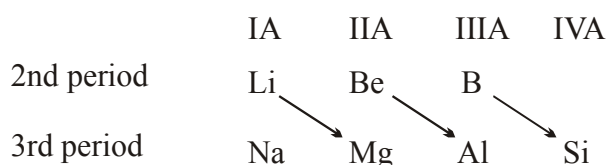
Group number for d block = number of $[ns + (n-1) d]$ electrons

Group number for f-block = 3

 **Use these carefully while locating the position.]**

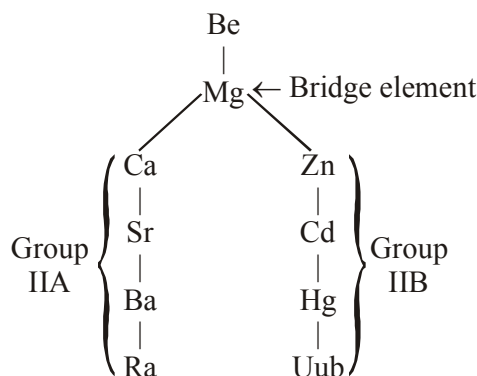
SOME COMMONLY USED TERMS

1. **Noble Gases** : Element of group 18 are called noble gases. These are also called as inert gases because their outermost ns and np orbitals are completely filled (except He and $1s^2$) and these gases are non-reactive in nature under ordinary conditions.
2. **Typical elements** : Elements of second and third period are known as typical elements.
3. **Diagonal relationship** : Properties of elements of second period resemble with the element of third period. This resemblance between properties of 2nd & 3rd period is called diagonal relationship.



4. Bridge elements :

The typical elements of third period are also called bridge elements as the division between two subgroups A and B starts from these elements. In second group Mg acts as a bridge element. The properties of bridge element are some what mixed of the elements of two subgroups as magnesium shows similarities with alkaline earth metals (IIA) on one hand and with zinc metals (IIB) on the other.



IUPAC NOMENCLATURE OF THE ELEMENT :

The names are derived by using roots for the three digits in the atomic number of the element and adding the ending -ium. The roots for the number are

Digit	Name	Abbreviation
0	nil	n
1	un	u
2	bi	b
3	tri	t
4	quad	q
5	pent	p
6	hex	h
7	sept	s
8	oct	o
9	enn	e

Thus element with atomic number 109 will be named as **une** (u for 1, n for 0 and e for 9). Table summarises the names of the elements with atomic number above 100.

PART-B (PERIODIC PROPERTIES)

PERIODICITY :

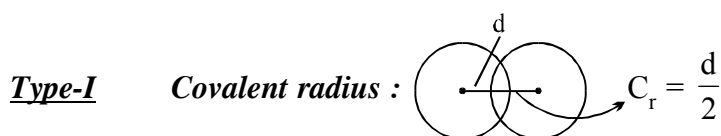
- (a) The regular gradation in properties from top to bottom in a group and from left to right in a period is called periodicity in properties.
- (b) In a period, the ultimate shell remain same, but the number of electrons gradually increases.
- (c) In a group, the number of electrons in the ultimate shell remains same, but the values of n increases.

Cause of periodicity

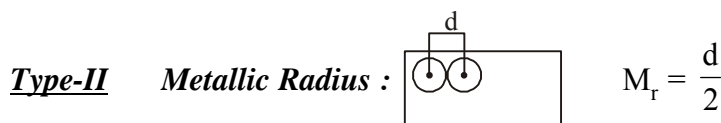
- (a) The cause of periodicity in properties is due to the same outermost shell electronic configuration repeating over regular intervals.
- (b) In the periodic table, elements with similar properties occur at intervals of 2, 8, 8, 18, 18 and 32. These numbers are called magic numbers.

ATOMIC RADIUS :

Since there is a problem in calculating actual size of atom, three types of radii can be defined :

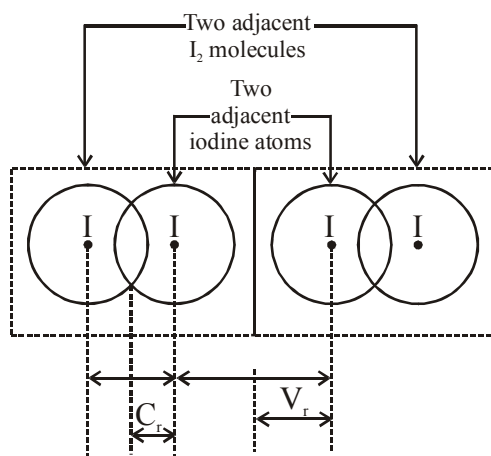


[Used for H_2 , Cl_2 and such molecules]



[Used for metals]

Type-III VanderWaal's Radius or Collision radius



VanderWaal's radius = $\frac{1}{2} \times$ Internuclear distance between nuclei of two neighbouring atoms belonging to nearest molecules.

VanderWaal's radius > Metallic radius > Covalent radius

The VanderWaal's radius and covalent radius of chlorine atom are 1.80 \AA and 0.99 \AA respectively.

Ionic Radius

A neutral atom changes to a cation by the loss of one or more electrons and to an anion by the gain of one or more electrons. The magnitude of charge on cation and anion is equal to the number of electrons lost or gained respectively. The ionic radii of the ions present in an ionic crystal may be calculated from the internuclear distance between the two ions.

(a) Radius of Cation

Radius of cation is smaller than that of corresponding atom. Since due to removal of electron(s), Z_{eff} increases.

(b) Radius of an Anion

Radius of an anion is invariably larger than that of the corresponding atom, since due to addition of electron(s) Z_{eff} decreases.

Factors affecting atomic radius:

- | | |
|--|--|
| (a) Z_{eff} increases, atomic radius decreases | $\text{Li} > \text{Be} > \text{B} > \text{C} > \text{N} > \text{O} > \text{F}$ |
| (b) Number of shell(n) increases, atomic radius increases | $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$ |
| (c) Screening effect increases, atomic radius increases. | |
| (d) Magnitude of -ve charge increases, atomic radius increases | $\text{O} < \text{O}^- < \text{O}^{2-}$ |
| (e) Magnitude of +ve charge increases, atomic radius decreases | $\text{Mn} > \text{Mn}^{+2} > \text{Mn}^{+3} > \text{Mn}^{+4}$ |
| (f) Bond order increases, atomic radius decreases | $>\text{N}-\text{N}< >-\text{N}=\text{N}- > \text{N}\equiv\text{N}$ |

Periodic Trend :


(a) For normal elements:

- (i) **Across a period :** It decreases from left to right in a period as Z_{eff} increases.

Ex. $\text{Ne} > \text{Li} > \text{Be} > \text{B} > \text{C} > \text{N} > \text{O} > \text{F}$

- (ii) **In a group :** It increases from top to bottom in a group as number of shells increases.

Ex. $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$

 **Note :** In III A group size of Al and Ga is nearly same (transition contraction)

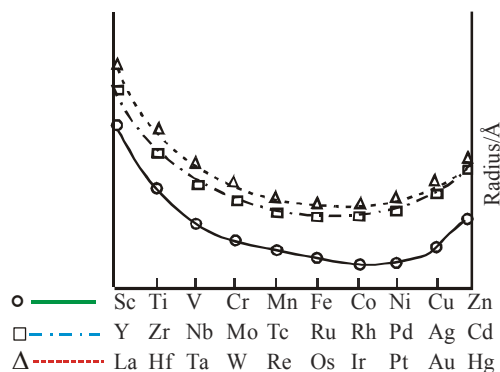
(b) For inert gases:

In respective period generally, the atomic radius of inert gas is largest, because for inert gas VanderWaal's radius is defined. The VanderWaal's radius of inert gases also increases on moving from top to bottom in the group.

(c) For transition elements:

From left to right in a period:

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic radius (Å)	1.44	1.32	1.22	1.17	1.17	1.17	1.16	1.15	1.17	1.25



Trends in atomic radii of transition elements

In a group :

- (i) The atomic radius of elements increases on moving down the first transition series (3d) to second transition series (4d). This is due to the increases in number of shells with the increase in atomic number.
- (ii) The atomic radii of second (4d) and third (5d) transition series in a group is almost same except Y(39) and La(57)

(d) For inner transition elements:

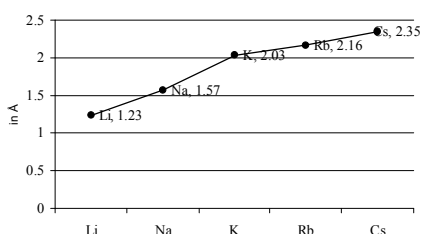
As we move along the lanthanide series, there is a decrease in atomic as well as ionic radius. The decrease in size is regular in ions but not so regular in atoms. This is called lanthanide contraction*.

Exceptions :

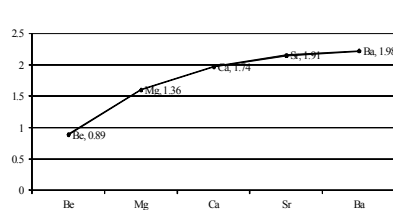
- (1) Noble gases have largest atomic sizes [Vander waal radii]. However, their covalent radii are smaller e.g. Xe.
- (2) Size of Ga and Al are same, [Z_{eff} increasing]
- (3) Size of Hf & Zr are same (lanthanide contraction)

Graphical representation of atomic radius :

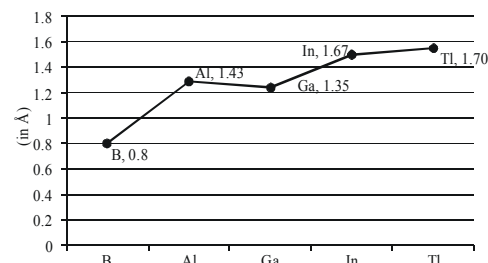
ALKALI METALS



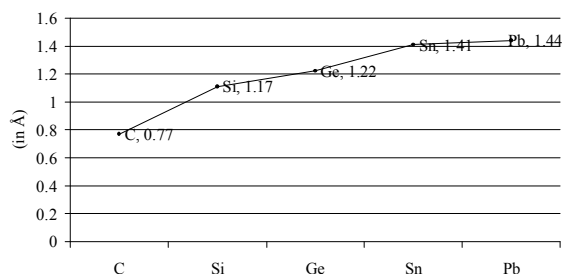
ALKALINE EARTH METALS



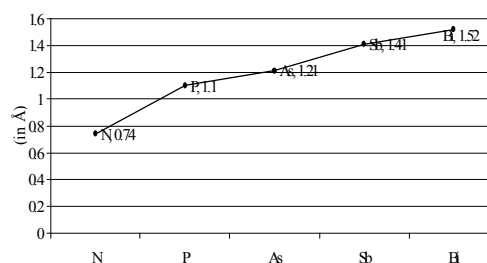
BORON FAMILY



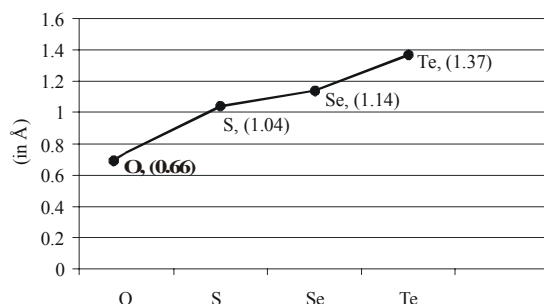
CARBON FAMILY



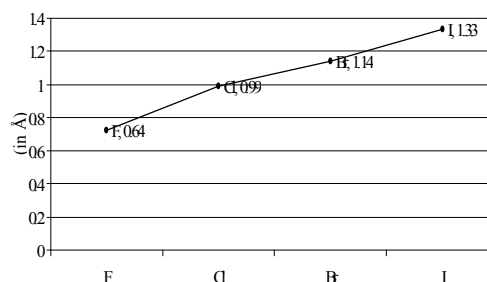
NITROGEN FAMILY (PNICOGENS)



CHALCOGENS



HALOGENS



☺ what can you predict or say about the increment in size along a group and decrement along a period]

ISOELECTRONIC MONOATOMIC SPECIES [$\text{Size} \propto 1/Z$] :

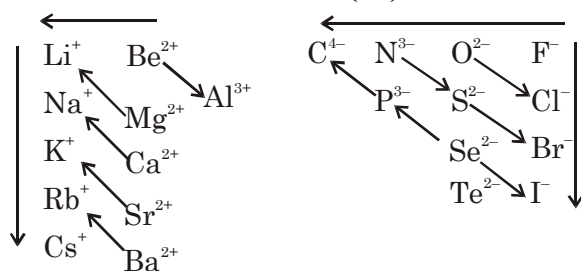
(i) S^{2-} , Cl^- , K^+ , Ca^{2+} , Sc^{3+}

(ii) H^- , He , Li^+

(iii) O^{2-} , F^- , Na^+ , Mg^{2+} , Al^{3+}

(iv) $\frac{\text{radius of cation}}{\text{radius of anion}} = \frac{Z_{\text{eff}} \text{ of Anion}}{Z_{\text{eff}} \text{ of Cation}}$

Note:- In the direction of arrow (\rightarrow) ionic size increases.

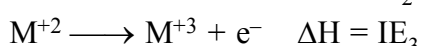
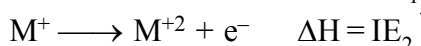
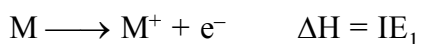


IONISATION ENERGY :

Amount of energy required to remove the most loosely bonded electron from an isolated gaseous atom from its ground state electronic configuration.

Units : kJ mol^{-1} , k cal mol^{-1} , eV per atom .

Ionisation is endothermic (endoergic) i.e. requires energy. Hence $\Delta H_{\text{ionisation}}$ is +ve.



Successive ionisation energy

$\text{IE}_3 > \text{IE}_2 > \text{IE}_1$ (always)

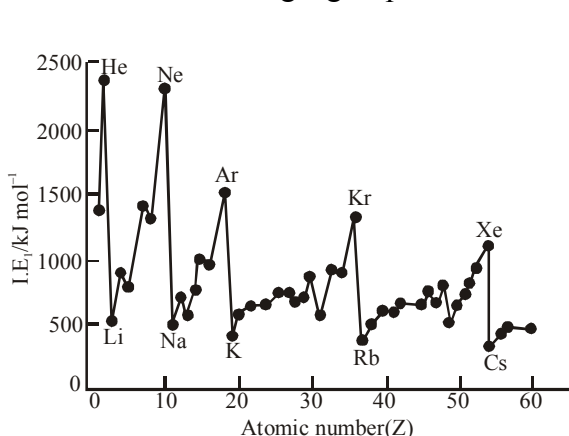
FACTORS AFFECTING IONISATION ENERGY :

- (1) Atomic size : Varies inversely
- (2) Screening effect : Varies inversely
- (3) Nuclear charge (Z) : Varies directly
- (4) Special electronic configuration of outermost electron (half filled / fully filled)
- (5) Type of orbitals involved in Ionisation : $s > p > d > f$.

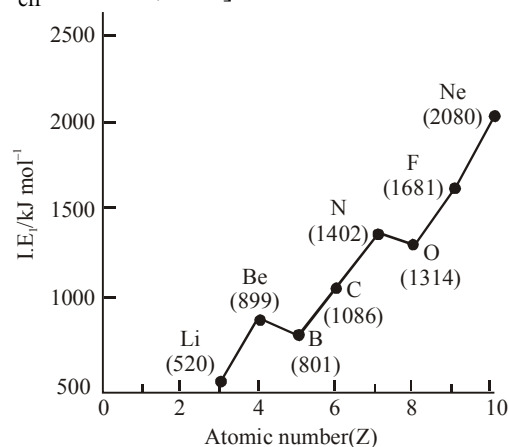
Note : Half filled and full filled inner orbitals, affects d-block and f-block trends.

General Trend: Along period I.E. increases [with some exception] [$Z_{\text{eff}} \uparrow$]

Along a group I.E. decrease [Z_{eff} constant, $n \uparrow$]



Variation of first ionization energy (IE_1) with atomic number for elements with $Z = 1$ to 60



First ionization energy (IE_1) of elements of the second period as a function of atomic number (Z)

Exception :

- (1) Along a period, half filled and fully filled configurations have higher I.E.
e.g. $\text{Be} > \text{B}$ and $\text{N} > \text{O}$.
- (2) Along a group, $\text{Ga} \approx \text{Al}$

PROPERTIES AFFECTED BY IONISATION ENERGY :

- (1) Metallic character (Varies inversely)
- (2) Reducing power (Varies inversely)
- (3) Tendency to stay in which state A^{+1} , A^{+2} or A^{+3}

 **Note :**

(a) Helium (He) has the highest ionisation energy (IE_1) among all the elements and Caesium (Cs) has the least (IE_1) value.

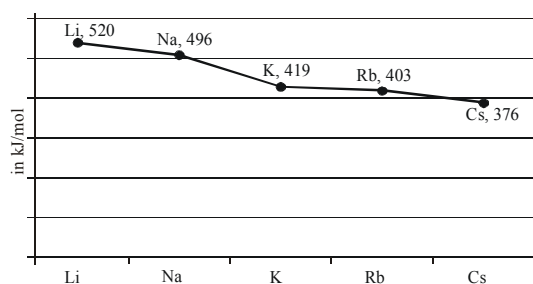
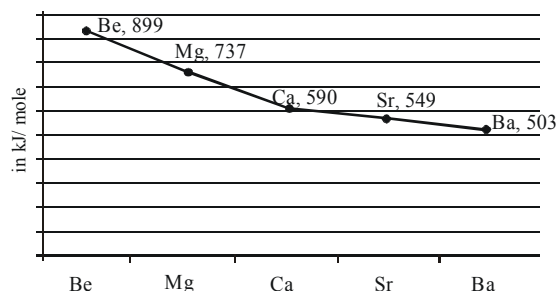
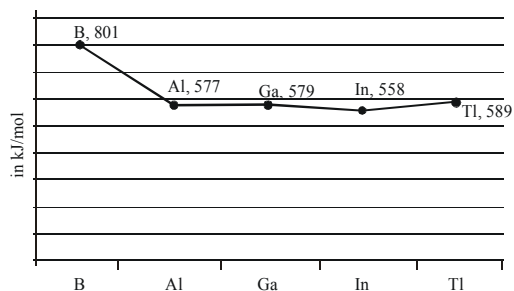
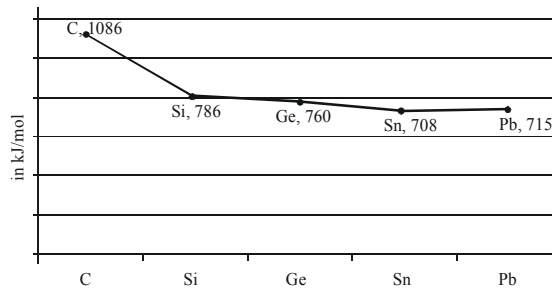
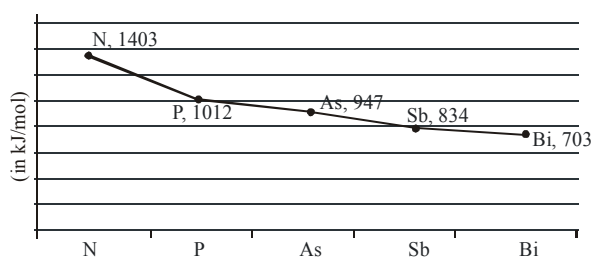
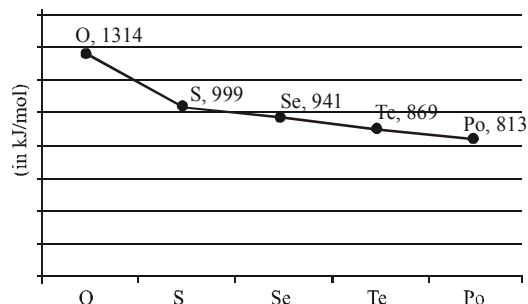
(b) Ionisation potential of inert gases is very high due to most stable s^2p^6 electronic configuration.

Element	He	Ne	Ar	Kr	Xe	Rn
IE_1 (eV)	24.5	21.6	15.8	14.0	12.1	10.7

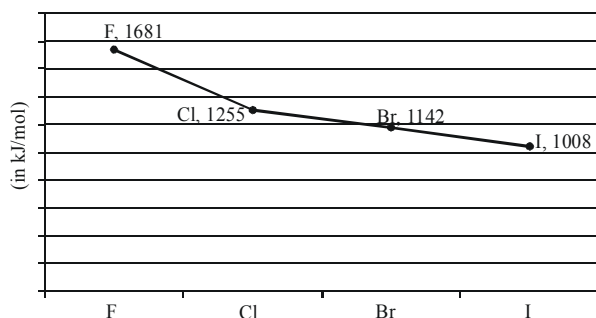
(c) For isoelectronic species I.E. increases with positive charge and decreases with negative charge.

e.g. $Al^{+3} > Mg^{+2} > Na^{+} > F^{-} > O^{-2} > N^{-3}$

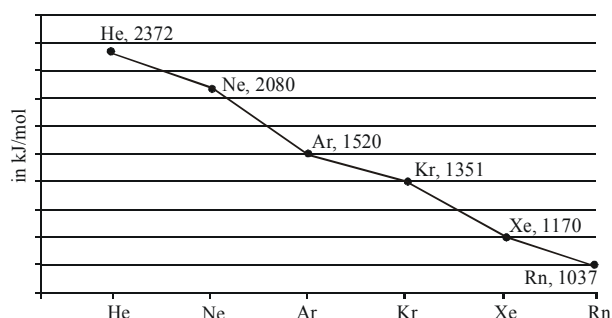
Graphical representation of ionisation energy :

ALKALI METALS**ALKALINE EARTH METALS****BORON FAMILY****CARBON FAMILY****NITROGEN FAMILY (PNICOGENS)****CHALCOGENS**

HALOGENS



NOBLE GASES



Ionisation energy of d-block elements :

1st, 2nd, 3rd IE's are increasing from left to right for 1st Transition series, but not regularly.

For 2nd IE Cr > Fe > Mn and Cu > Zn

For 3rd IE Mn > Cr > Fe and Zn has highest.

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic number	21	22	23	24	25	26	27	28	29	30
Electronic configuration										
M	3d ¹ 4s ²	3d ² 4s ²	3d ³ 4s ²	3d ⁵ 4s ¹	3d ⁵ 4s ²	3d ⁶ 4s ²	3d ⁷ 4s ²	3d ⁸ 4s ²	3d ¹⁰ 4s ¹	3d ¹⁰ 4s ²
M ²⁺	3d ¹	3d ²	3d ³	3d ⁴	3d ⁵	3d ⁶	3d ⁷	3d ⁸	3d ⁹	3d ¹⁰
M ³⁺	[Ar]	3d ¹	3d ²	3d ³	3d ⁴	3d ⁵	3d ⁶	3d ⁷	—	—
Enthalpy of atomisation, Δ _a H ^o /kJ mol ⁻¹	326	473	515	397	281	416	425	430	339	126
Ionisation Enthalpy, Δ ₁ H ^o /kJ mol ⁻¹										
I	631	656	650	653	717	762	758	736	745	906
II	1235	1309	1414	1592	1509	1561	1644	1752	1958	1734
III	2393	2657	2833	2990	3260	2962	3243	3402	3556	3829

ELECTRON AFFINITY & ELECTRON GAIN ENTHALPY (EGE) :

Electron Affinity : Amount of energy released when an electron is added to an isolated gaseous atom.

Units : k J mol⁻¹ , k Cal mol⁻¹ and eV per atom.

Addition of electron results in release of energy in most of the cases but for addition of second electron energy is always required. The sum of EA₁ & EA₂ is +ve (energy required)

$$E A \propto \frac{1}{\text{atomic size}} \propto Z_{\text{eff}} \quad (\text{Cl has the highest E.A.})$$

Electron gain Enthalpy (EGE) : When expressed in terms of enthalpy change (ΔH_{eg}) then it is termed as EGE Remember that ΔH = – ve for exothermic change.

For EA₁, energy is released

$$\therefore \Delta H_{\text{eg1}} = - \text{ve (Not always)}$$

For EA₂, EA₃energy is required

$$\therefore \Delta H_{\text{eg2}} = + \text{ve (always)}$$

In general EA₁ + EA₂ , energy is required.

$$\therefore (\Delta H_{\text{eg1}} + \Delta H_{\text{eg2}}) > 0$$

Note : ΔH_{eg} ≈ – EA

FACTORS AFFECTING ELECTRON AFFINITY :

- (1) **Atomic size** : Varies inversely
- (2) **Nuclear charge** : Varies directly
- (3) For stable electronic configuration i.e. half filled and fully filled shells EA decreases.

General Trend : Along a period, electron affinity increases [with a few exceptions] as $Z_{\text{eff}} \uparrow$.

Along a group, electron affinity decreases after 3rd period. Between 2nd and 3rd period in p block electron affinity of 2nd period is lesser.

Exception :

- (1) A fully filled and half filled configuration have low values of EA or even sometimes energy is required rather than getting released.
- (2) 2nd period has lower value than 3rd owing to repulsion between electrons in small sized 2nd period elements.

Electron affinity of the main-group elements (in electron volts)

1							18
H							He
+0.754	2	13	14	15	16	17	-0.5
Li	Be	B	C	N	O	F	Ne
+0.618	≤ 0	$\leq +0.277$	+1.263	-0.07	+1.461	+3.399	-1.2
Na	Mg	Al	Si	P	S	Cl	Ar
+0.548	≤ 0	+0.441	+1.385	+0.747	+2.077	+3.617	-1.0
K	Ca	Ga	Ge	As	Se	Br	Kr
+0.502	-	+0.03	+1.2	+0.81	+2.021	+3.365	-1.0
Rb	Sr	In	Sn	Sb	Te	I	Xe
+0.486	-	+0.3	+1.2	+1.07	+1.971	+3.059	-0.8

ELECTRO NEGATIVITY :**Property of an atom in a molecule**

F has highest electronegativity in the periodic table.

Decreasing order $\rightarrow F > O > Cl \approx N > Br > S \approx C > I > H$.

Pauling Scale : $X_A \sim X_B = 0.208\sqrt{\Delta_{A-B}}$ Δ in kcal/mol

$$X_A \sim X_B = 0.102 \sqrt{\Delta_{A-B}} \quad \Delta \text{ in kJ/mol}$$

$$\Delta_{A-B} = E_{A-B} - (E_{A-A} \times E_{B-B})^{1/2}$$

Where, E_{A-B} = Bond energy of A-B; E_{A-A} = Bond energy of A-A; E_{B-B} = Bond energy of B-B

Mulliken's Scale : $X_M = \frac{IP + EA}{2}$ (IP & EA are expressed in eV)

Mulliken's values of EN are about 2.8 times higher than values on Pauling's scale.

$$\text{i.e. } X_P = \frac{X_M}{2.8}$$

$$\text{Allred-Rochow's Scale : } X_{\text{AR}} = \frac{0.359Z_{\text{eff}}}{r^2} ; X_{\text{P}} = X_{\text{AR}} + 0.744$$

r = covalent radius of atom (in Å)

Z_{eff} = Effective nuclear charge on periphery


FACTORS AFFECTING ELECTRO NEGATIVITY :

- (1) **Nuclear attraction** : Varies directly
- (2) **Atomic radius** : Varies inversely
- (3) **Charge on ions** : More positive charge, more electronegativity and more -ve charge, less electronegativity.
- (4) **Hybridisation** : To be discussed later in chemical bonding chapter.

General Trends : Along a period, electronegativity increases

Along a group, electronegativity decreases

Exceptions : Not Noteworthy.

 **Note:** Electronegativity of $\text{F} > \text{Cl}$ but Electron affinity of $\text{Cl} > \text{F}$
Electronegativity of Some Elements (on Pauling's Scale)

H 2.1						
Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
Cs 0.7	Ba 0.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2
Fr 0.7	Ra 0.9					

In **Pauling's Scale**, elements having almost same electronegativity are-

$$\text{C} \approx \text{S} \approx \text{I} \approx 2.5$$

$$\text{N} = \text{Cl} = 3.0$$

$$\text{P} = \text{H} = 2.1$$

$$\text{Cs} = \text{Fr} = 0.7$$

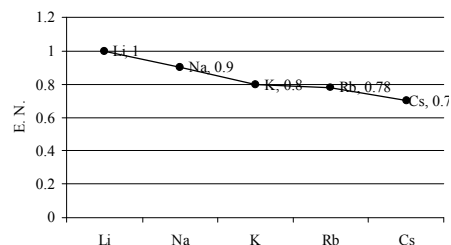
$$\text{Be} = \text{Al} = 1.5$$

PROPERTIES DEPENDENT ON ELECTRO NEGATIVITY :

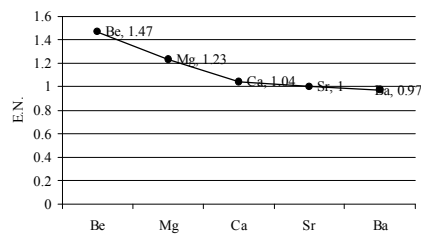
- (1) % ionic character
- (2) Strength of bond
- (3) Bond Length
- (4) Nature of hydrides
- (5) Nature of hydroxide.

Graphical representation of Electronegativity :

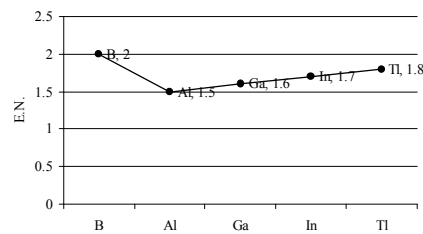
ALKALI METALS



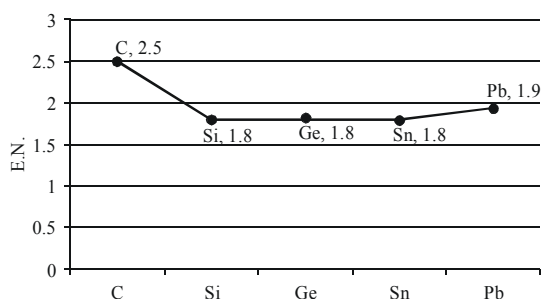
ALKALINE EARTH METALS



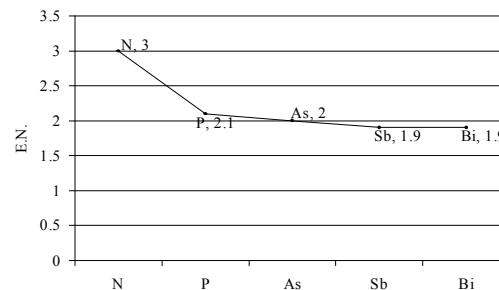
BORON FAMILY



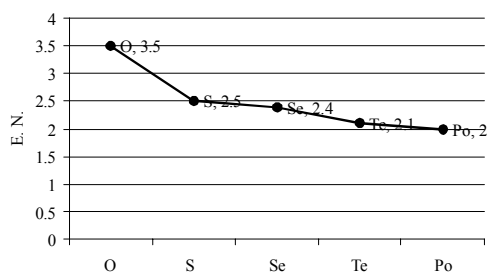
CARBON FAMILY



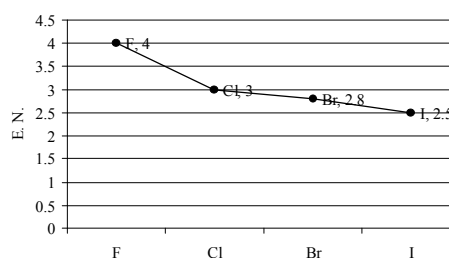
NITROGEN FAMILY (PNICOGENS)



CHALCOGENS



HALOGENS



LATTICE ENERGY :

The amount of energy released during the formation of 1 mole crystal lattice from constituent gaseous ions.



OR

The lattice energy of an ionic compound is the energy required to separate 1 mole of solid ionic substance completely into gaseous ions.



Lattice energies are large and positive because of attraction between positive and negative ions. The potential energy of two interacting charged particles is given by:

$$E = K \frac{Q_1 Q_2}{r}$$

where, $r = r^+ + r^-$; $r^+ \rightarrow$ radius of cation, $r^- \rightarrow$ radius of anion

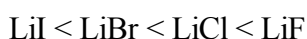
Where Q_1 and Q_2 are the charge on the particles in coulombs, and r is the distance between their centres in meters. The constant K has the value $9.0 \times 10^9 \text{ J} - \text{m/C}^2$.

Factors affecting lattice energy :

- The lattice energy increases as the charge on the ions increases and as their radii decreases.
- The magnitude of lattice energies however depends primarily on the ionic charges because ionic radii do not vary over a wide range.

For Example :

The lattice energy order for some compounds is given below.

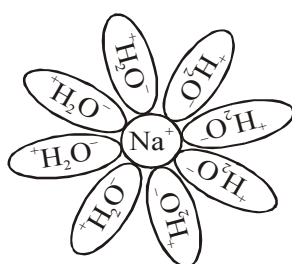
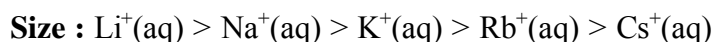


(Due to small size of halide ion F^- alongwith small Li^+)

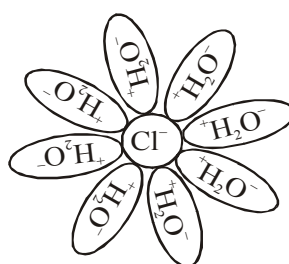
HYDRATION ENERGY :

It is the energy released when 1 mol of gaseous ions are hydrated in water. It is directly proportional to nuclear charge and inversely proportional to size. It always decreases down the group.

- As the charge density of ion increases hydrated size (or aqueous radius) increases.

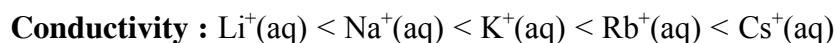
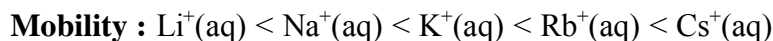


Hydration of Na^+



Hydration of Cl^-

- As the hydrated size of ion increases ionic mobility decreases, which thus, decreases conductivity of ions.



- Hydration energy also affects the solubility of ionic compounds. If hydration energy is greater than lattice energy then ionic compound will be soluble in water. More is the hydration energy, greater is the solubility, whereas, if lattice energy decreases, solubility of ionic compound increases.

MISCELLANEOUS CHEMICAL PROPERTIES :

1. Periodicity of hydra acids :

- (a) Acidic character of hydra acid increases from left to right in a period.
- (b) Acidic character of hydra acid increases from top to bottom in a group.

2. Periodicity of oxy acids :

- (a) Acidic character of oxy acid increases from left to right in a period.
- (b) Acidic character of oxy acid decreases from top to bottom in a group.

3. Periodicity of nature of oxide :

- (a) On moving from left to right in a period acidic nature of oxide generally increases.
e.g. $\text{CO}_2 < \text{P}_2\text{O}_5 < \text{SO}_3 < \text{Cl}_2\text{O}_7$
- (b) On moving from top to bottom in a group acidic nature of oxide generally decreases.

4. General trends

- (a) **Hydration energy** decreases along a group.
- (b) **Lattice energy** decreases along a group.

:: Some points to Remember ::

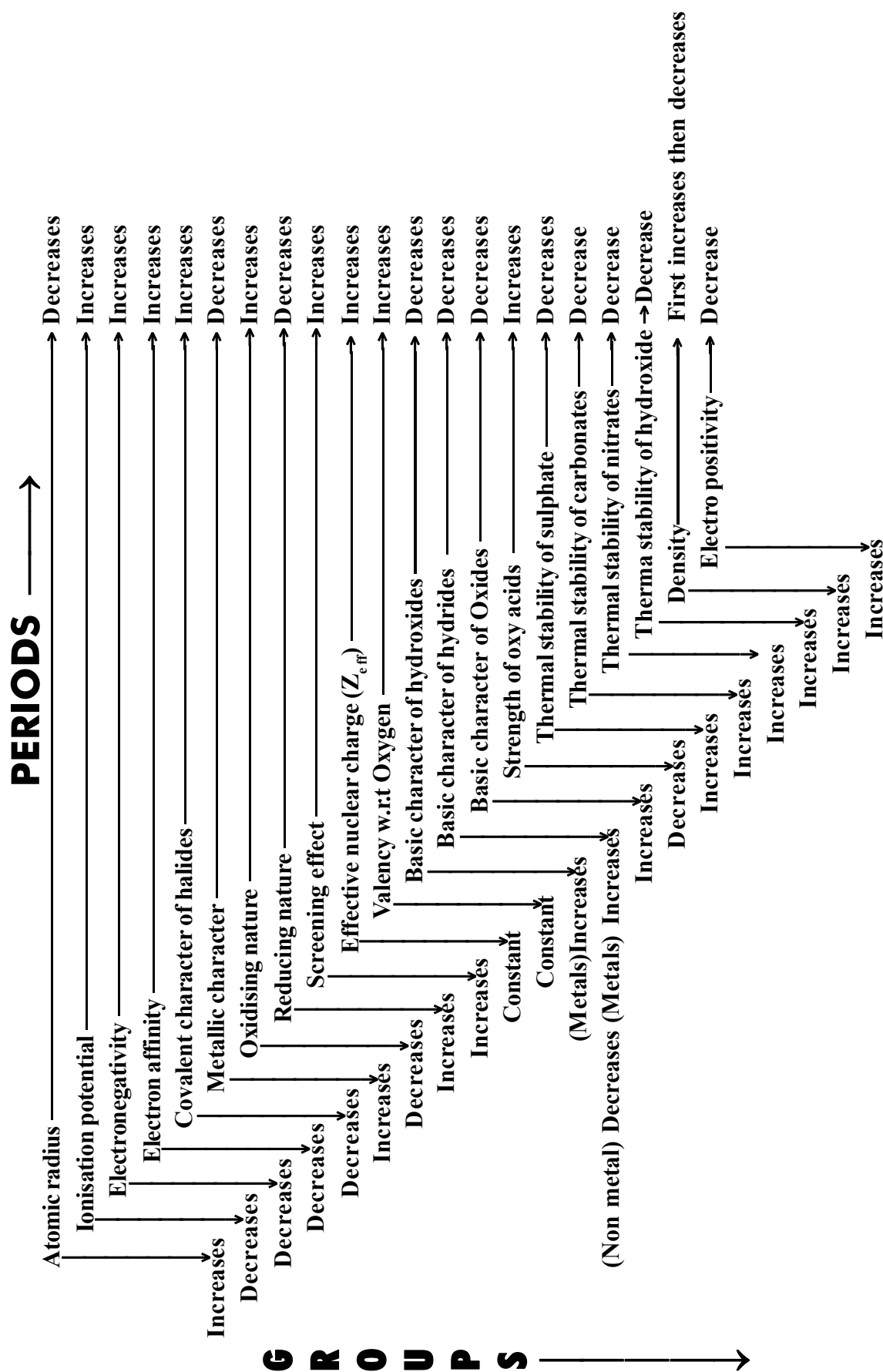
(without considering radioactive elements)

1. Second most electronegative element is Oxygen
2. Hydrogen is the lightest element and Lithium is lightest metal.
3. Helium has the highest value of I.P.
4. In periodic table metalloids are only in p-block.
5. Total gaseous elements are 11 (He, Ne, Ar, Kr, Xe, Rn, H₂, N₂, O₂, Cl₂, F₂)
6. Liquid metal at room temperature is – Hg.
7. Diamond is hardest natural substance.
8. Halogens have highest electron affinity and amongst them, Cl has the highest amongst them.
9. The largest cation of the periodic table = Cs⁺.
10. The smallest cation of the periodic table = H⁺.
11. The smallest anion of the periodic table = F⁻.
12. The biggest element of periodic table = Fr.
13. The smallest element of periodic table = H.
14. Br is liquid non-metal element at room temperature.
15. Osmium is the heaviest element known.
16. Fluorine is the most electronegative element.

Extended or Long Form of the Periodic Table

		s-Block Elements										p-Block Elements										d-Block Elements										f-Block Elements																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																													
		IA (1)		IIA (2)				IIIB (3)		IVB (4)		VB (5)		VIB (6)		VIIB (7)		VIII (8)		IX (9)		X (10)		XI (11)		XII (12)				IIIA (13)		IVA (14)		VA (15)		VIA (16)		VIIA (17)		He (18)																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																					
Period	↓	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																					
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GENERAL TRENDS OF DIFFERENT PROPERTIES IN THE PERIOD AND GROUPS



EXERCISE # O-1

Periodic Table

- Which is not anomalous pair of elements in the Mendeleev's periodic table:-
(A) Ar and K (B) Co and Ni (C) Te and I (D) Al and Si
- Representative elements belong to :
(A) s-and p-block (B) d-block (C) d and f-block (D) f-block
- True statement is :-
(A) All the transuranic elements are synthetic elements
(B) Elements of third period are called transition elements
(C) Element of $[\text{Ar}] 3d^{10}4s^2$ configuration is placed in IIA group
(D) Electronic configuration of elements of a group is same
- Which of the following match is correct :-
(A) Last natural element – Uub
(B) General electronic configuration of IA group – ns^2
(C) Inert gas elements lies between 2nd – 6th period
(D) Typical elements – 3rd period elements
- The electronic configuration of elements X and Z are $1s^2 2s^2 2p^6 3s^2 3p^5$ and $1s^2 2s^2 2p^5$ respectively. What is the position of element X with respect to position of Z in the periodic table -
(A) Just below element Z (B) Just above Z
(C) Left to the Z (D) right to the Z
- Which of the following is not a Dobereiner triad :
(A) H, F, Cl (B) N, O, F (C) P, As, Sb (D) S, Se, Te
- Select the incorrect statement for Lothar Meyer's curve :
(A) Curve is plotted between atomic weight and atomic volume
(B) Alkali metals occupy maxima of curve
(C) Halogens occupy descending portions of the curve
(D) Transition metals occupy bottom portions of the curve

Atomic & Ionic Radii

- The size of the following species increases in the order:
(A) $\text{Mg}^{2+} < \text{Na}^+ < \text{F}^-$ (B) $\text{F}^- < \text{Na}^+ < \text{Mg}^{2+}$
(C) $\text{Mg}^{2+} < \text{F}^- < \text{Na}^+$ (D) $\text{Na}^+ < \text{F}^- < \text{Mg}^{2+}$
- Highest size will be of
(A) Br^- (B) I (C) I^- (D) I^+
- Element Cu has two oxidation states Cu^{+1} & Cu^{+2} . the right order of radii of these ions.
(A) $\text{Cu}^{+1} > \text{Cu}^{+2}$ (B) $\text{Cu}^{+2} > \text{Cu}^{+1}$ (C) $\text{Cu}^{+1} = \text{Cu}^{+2}$ (D) $\text{Cu}^{+2} \geq \text{Cu}^{+1}$
- The correct order of increasing atomic size of element N, F, Si & P.
(A) $\text{N} < \text{F} < \text{Si} < \text{P}$ (B) $\text{F} > \text{N} < \text{P} < \text{Si}$ (C) $\text{F} < \text{N} < \text{P} < \text{Si}$ (D) $\text{F} < \text{N} < \text{Si} < \text{P}$
- The correct order of atomic or ionic size
(A) $\text{N} < \text{Li} < \text{B}$ (B) $\text{Cl} < \text{Mg} < \text{Ca}$ (C) $\text{Ca}^{+2} < \text{S}^{-2} < \text{Cl}^-$ (D) $\text{Na}^+ < \text{Mg}^{+2} < \text{Cl}^-$
- In isoelectronic series largest difference between size is observed in N^{3-} , O^{2-} , F^- , Na^+ , Mg^{2+} :
(A) N^{3-} , Mg^{2+} (B) N^{3-} , O^{2-} (C) Mg^{2+} , Na^+ (D) F^- , Na^+

14. Mg, Mg^{2+} , Al and Al^{3+} are arranged in decreasing order of size $1 > 2 > 3 > 4$. Species which are present at 1 and 4 position respectively are :

(A) Al, Mg^{2+} (B) Mg, Al^{3+} (C) Mg^{2+} , Al (D) Al^{3+} , Mg

Ionization Energy or Potential

15. In which of the following electronic configuration, ionisation energy will be maximum in
(A) $[Ne] 3s^2 3p^1$ (B) $[Ne] 3s^2 3p^2$ (C) $[Ne] 3s^2 3p^3$ (D) $[Ar] 3d^{10} 4s^2 4p^3$
16. The correct order of second ionisation potential of C, N, O and F is:
(A) $C > N > O > F$ (B) $O > N > F > C$ (C) $O > F > N > C$ (D) $F > O > N > C$
17. The ionization energy will be maximum for which process?
(A) $Ba \rightarrow Ba^+$ (B) $Be \rightarrow Be^+$ (C) $Cs \rightarrow Cs^+$ (D) $Li \rightarrow Li^+$
18. Amongst the following, the incorrect statement is
(A) $IE_1 (Al) < IE_1 (Mg)$ (B) $IE_1 (Na) < IE_1 (Mg)$
(C) $IE_2 (Mg) > IE_2 (Na)$ (D) $IE_3 (Mg) > IE_3 (Al)$
19. Decreasing ionization potential for K, Ca & Ba is
(A) $Ba > K > Ca$ (B) $Ca > Ba > K$ (C) $K > Ba > Ca$ (D) $K > Ca > Ba$
20. Alkaline earth metals always form dipositive ions due to
(A) $IE_2 - IE_1 > 10 \text{ eV}$ (B) $IE_2 - IE_1 = 17 \text{ eV}$
(C) $IE_2 - IE_1 < 10 \text{ eV}$ (D) None of these
21. The correct order of second I.P.
(A) $Na < Mg > Al < Si$ (B) $Na > Mg < Al > Si$
(C) $Na > Mg > Al < Si$ (D) $Na > Mg > Al > Si$

Electron affinity or Electron Gain Enthalpy

22. The process requires absorption of energy is
(A) $F \rightarrow F^-$ (B) $Cl \rightarrow Cl^-$ (C) $O^- \rightarrow O^{2-}$ (D) $H \rightarrow H^-$
23. Of the following elements, which possesses the highest electron affinity?
(A) As (B) O (C) S (D) Se
24. Electron affinities of O, F, S and Cl are in the order.
(A) $O < S < Cl < F$ (B) $O < S < F < Cl$
(C) $S < O < Cl < F$ (D) $S < O < F < Cl$
25. Increasing order of Electron affinity for following configuration.
(a) $1s^2, 2s^2 2p^2$ (b) $1s^2, 2s^2 2p^4$
(c) $1s^2, 2s^2 2p^6 3s^2 3p^4$ (d) $1s^2, 2s^2 2p^6, 3s^2 3p^3$
(A) $d < a < b < c$ (B) $d < a < c < b$ (C) $a < b < c < d$ (D) $a < b < d < c$
26. Highest electron affinity is shown by
(A) F^- (B) Cl^- (C) Li^+ (D) Na^+
27. Which of the following statements is not true?
(A) F atom can hold additional electron more tightly than Cl atom
(B) Cl atom can hold additional electron more tightly than F atom
(C) The incoming electron encounters greater repulsion for F atom than for Cl atom
(D) It is easier to remove an electron from F^- than Cl^- .

Electronegativity

28. The outermost electronic configuration of most electronegative element amongst the following is :
 (A) $ns^2 np^3$ (B) $ns^2 np^4$ (C) $ns^2 np^5$ (D) $ns^2 np^6$
29. In the following, which is the correct representation ?
 (A) $\overset{\delta+}{C} - \overset{\delta-}{F}$ (B) $\overset{\delta+}{C} - \overset{\delta+}{Cl}$ (C) $\overset{\delta+}{F} - \overset{\delta-}{Cl}$ (D) $\overset{\delta-}{O} - \overset{\delta+}{F}$
30. On the Pauling's electronegativity scale, which element is next to F .
 (A) Cl (B) O (C) Br (D) Ne
31. Which one is not correct order of electronegativity.
 (A) $F > Cl > Br > I$ (B) $Si > Al > Mg > Na$
 (C) $Cl > S > P > Si$ (D) None of these
32. The increasing order of acidic nature of Li_2O , BeO , B_2O_3
 (A) $Li_2O > BeO < B_2O_3$ (B) $Li_2O < BeO < B_2O_3$
 (C) $Li_2O < BeO > B_2O_3$ (D) $Li_2O > BeO > B_2O_3$
33. The lowest electronegativity of the element from the following atomic number is.
 (A) 37 (B) 55 (C) 9 (D) 35

Miscellaneous

34. Which of the following does not reflect the periodicity of element
 (A) Bonding behaviour (B) Electronegativity
 (C) Ionisation potential (D) Neutron/ Proton ratio
35. Among the following, which species is/are paramagnetic ?
 (i) Sr^{2+} (ii) Fe^{3+} (iii) Co^{2+} (iv) S^{2-} (v) Pb^{2+}
 (A) i, iv, v (B) i, ii, iii (C) ii, iii (D) iv, v
36. Choose the s-block element from the following:
 (A) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^5, 4s^1$ (B) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^1$
 (C) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$ (D) all of the above
37. False statement for periodic classification of elements is
 (A) The properties of the elements are periodic function of their atomic numbers.
 (B) No. of non-metallic elements is less than the no. of metallic elements.
 (C) First ionization energy of elements does not increase regularly with the increase in atomic number in a period.
 (D) d-subshell is filled by final electron with increasing atomic number of inner transition elements.
38. Which of the following order is incorrect against the property indicated :
 (A) $Mg < Ar < Na$ (2nd I.E.) (B) $Be < F < Cl$ ($|\Delta H_{eg}|$)
 (C) $Rb < Na < K > Ca$ (atomic radius) (D) $P < S < N$ (electronegativity)
39. If each orbital can hold a maximum of three electrons, the number of elements in 9th period of periodic table (long form) will be
 (A) 48 (B) 162 (C) 50 (D) 75

40. Which of the following element has highest metallic character .

Element	IP
(A) P	17 eV
(B) Q	2 eV
(C) R	10 eV
(D) S	13 eV

41. The electronic configuration of an element is $1s^2 2s^2 2p^6 3s^2 3p^4$. The atomic number and the group number of the element 'X' which is just below the above element in the periodic table are respectively.

- (A) 24 & 6 (B) 24 & 15 (C) 34 & 16 (D) 34 & 8

42. The number of d- electrons in Mn^{2+} is equal to that of

- (A) p-electrons in N (B) s-electrons in Na
(C) d-electrons in Fe^{+2} (D) p-electrons in O^{-2}

43. Which of the following formula has involved all the energy terms used to calculated ΔH_f° of $Na_2O_{(s)}$.
(ΔH_{sb} : Sublimation energy ; $I.E_1$: First ionisation energy ; $I.E_2$: Second ionisation energy ; B.D.E.; Bond dissociation energy ; E.G.E₁ : First electron gain enthalpy ; E.G.E₂ : Second electron gain enthalpy; U : Lattice energy)

(A) $+ 2\Delta H_{sb} + I.E_1 + I.E_2 + \frac{B.D.E.}{2} + E.G.E_1 + E.G.E_2 + U$

(B) $+ 2\Delta H_{sb} + 2I.E_1 + \frac{B.D.E.}{2} + E.G.E_1 + E.G.E_2 + U$

(C) $+ 2\Delta H_{sb} + 2I.E_1 + \frac{B.D.E.}{2} + 2E.G.E_1 + U$

(D) $+ 2\Delta H_{sb} + I.E_1 + \frac{B.D.E.}{2} + E.G.E_1 + E.G.E_2 + U$

44. EN of the element (A) is E_1 and IP is E_2 . Hence EA will be according to mulliken

- (A) $2E_1 - E_2$ (B) $E_1 - E_2$ (C) $E_1 - 2E_2$ (D) $(E_1 + E_2)/2$

45. Moving from right to left in a periodic table, the atomic size is:

- (A) Increased (B) Decreased (C) Remains constant (D) None of these

46. One element has atomic weight 39. Its electronic configuration is $1s^2, 2s^2 2p^6, 3s^2 3p^6 4s^1$. The true statement for that element is:

- (A) High value of IE (B) Transition element (C) Isotone with $^{38}_{18}Ar$ (D) None

47. The number of paired electrons in oxygen atom is:

- (A) 6 (B) 16 (C) 8 (D) 32

48. The decreasing size of K^+ , Ca^{+2} , Cl^- & S^{2-} follows the order:

- (A) $K^+ > Ca^{+2} > S^{2-} > Cl^-$ (B) $K^+ > Ca^{+2} > Cl^- > S^{2-}$
(C) $Ca^{+2} > K^+ > Cl^- > S^{2-}$ (D) $S^{2-} > Cl^- > K^+ > Ca^{+2}$

49. Which of the following has the maximum number of unpaired electrons

- (A) Mg^{2+} (B) Ti^{3+} (C) V^{3+} (D) Fe^{2+}

EXERCISE : O-2

Atomic & Ionic Radius

- Select correct order of size :
 (A) $\text{Ti}^{2+} < \text{Ti} < \text{Zr}$ (B) $\text{Ti}^{2+} < \text{Ti} < \text{Hf}$ (C) $\text{Zr}^{2+} < \text{Zr} \approx \text{Hf}$ (D) $\text{Hf}^{2+} < \text{Hf} \approx \text{Zr}$
- Which of the following orders of atomic / Ionic radius is correct ?
 (A) $\text{B} < \text{Al} \approx \text{Ga}$ (B) $\text{Sc} > \text{Cu} < \text{Zn}$ (C) $\text{C} < \text{O} < \text{N}$ (D) $\text{Al}^{3+} < \text{Al}^{2+} < \text{Al}^+$

Electron Affinity

- Which of the following is correct order of EA.
 (A) $\text{N} < \text{C} < \text{O} < \text{F}$ (B) $\text{F} > \text{Cl} > \text{Br} > \text{I}$ (C) $\text{Cl} > \text{F} > \text{Br} > \text{I}$ (D) $\text{C} < \text{N} < \text{O} < \text{F}$
- The electron affinity of the members of oxygen family of the periodic table, follows the sequence
 (A) $\text{O} > \text{S} > \text{Se}$ (B) $\text{S} > \text{O} < \text{Se}$ (C) $\text{O} < \text{S} > \text{Se}$ (D) $\text{Se} > \text{O} > \text{S}$

Ionisation Energy

- Considering the following ionisation steps :
 $\text{A(g)} \rightarrow \text{A}^+(\text{g}) + \text{e}^- \quad \Delta H = 100 \text{ eV}$ $\text{A(g)} \rightarrow \text{A}^{2+}(\text{g}) + \text{e}^- \quad \Delta H = 250 \text{ eV}$
 Select the correct statements :
 (A) IE_1 of A(g) is 100 eV (B) IE_1 of $\text{A}^+(\text{g})$ is 150 eV
 (C) IE_2 of A(g) is 150 eV (D) IE_2 of A(g) is 250 eV
- Which of the following are correct ?
 (A) $\text{IE}_2(\text{Mg}) < \text{IE}_2(\text{Na})$ (B) $\text{EA}(\text{N}) < \text{EA}(\text{P})$
 (C) Atomic size $\text{Mg}^{2+} > \text{Atomic size}(\text{Li}^+)$ (D) $\text{IP of Na} < \text{Mg} < \text{Al}$

Electronegativity

- Amongst the following statements, which is / are correct?
 (A) Electronegativity of sulphur is greater than that of oxygen.
 (B) Electron affinity of oxygen is smaller than that of sulphur.
 (C) Electron gain enthalpy of fluorine is most negative
 (D) Electron gain enthalpy of chlorine is most negative
- An element 'E' have $\text{IE} = x \text{ eV/atom}$ and $\text{EA} = y \text{ eV / atom}$ and EN on Pauling scale is 1.2. Find EN of 'E' on Mullikan scale :

$$(A) \frac{x+y}{2} \quad (B) 1.2 \times 2.8 \quad (C) \frac{x+y}{2.8} - 1.2 \quad (D) 1.2 - \frac{x+y}{2}$$

Hydration Energy

- Choose the INCORRECT order of hydrated size of the ions -
 (A) $\text{F}_{(\text{aq.})}^{\ominus} > \text{Cl}_{(\text{aq.})}^{\ominus} > \text{Br}_{(\text{aq.})}^{\ominus} > \text{I}_{(\text{aq.})}^{\ominus}$ (B) $\text{Rb}_{(\text{aq.})}^{\oplus} > \text{K}_{(\text{aq.})}^{\oplus} > \text{Na}_{(\text{aq.})}^{\oplus} > \text{Li}_{(\text{aq.})}^{\oplus}$
 (C) $\text{Na}_{(\text{aq.})}^{\oplus} > \text{Mg}_{(\text{aq.})}^{2+} > \text{Al}_{(\text{aq.})}^{3+}$ (D) $\text{Be}_{(\text{aq.})}^{2+} > \text{Mg}_{(\text{aq.})}^{2+} > \text{Ca}_{(\text{aq.})}^{2+} > \text{Sr}_{(\text{aq.})}^{2+}$
- Find the correct ionic mobility order in aqueous solution from the following options-
 (A) $\text{Li}^+ < \text{Na}^+$ (B) $\text{Mg}^{2+} < \text{Sr}^{2+}$ (C) $\text{Na}^+ < \text{K}^+$ (D) $\text{F}^- < \text{Cl}^-$

Miscellaneous

11. Select the correct statement(s).
 - (A) The value of electron gain enthalpy of an element can be -ve or +ve.
 - (B) In the periodic table, metallic character of the elements increases down the group and decreases across the period
 - (C) The Cl^- & S^{2-} are isoelectronic species but first one is not smaller in size than the second
 - (D) Ionization enthalpy of an atom is equal to electron gain enthalpy of cation
12. In halogens, which of the following properties increase from iodine to fluoroine
 - (A) Ionisation energy
 - (B) Electronegativity
 - (C) Bond length
 - (D) Electron affinity
13. In which of the following set of elements 1st element is more metallic than second.
 - (A) Ba, Ca
 - (B) Sb, Sn
 - (C) Ge, S
 - (D) Na, F
14. Which of the following order(s) is / are **CORRECT** :
 - (A) $\text{Li} < \text{Be} < \text{B} < \text{C}$ (IE_1)
 - (B) $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$ (Bond length)
 - (C) $\text{Na}_2\text{O} < \text{MgO} < \text{Al}_2\text{O}_3 < \text{SiO}_2 < \text{P}_2\text{O}_5$ (Acidic)
 - (D) $\text{Li}^+(\text{g}) < \text{Na}^+(\text{g}) < \text{K}^+(\text{g}) < \text{Cs}^+(\text{g})$ (Ionic radius)
15. Which of the following order is correct :
 - (A) $\text{P} < \text{Si} < \text{Be} < \text{Mg} < \text{Na}$ (Metallic character)
 - (B) $\text{Mg}^{+2} < \text{Na}^+ < \text{F}^- < \text{O}^{2-}$ (Ionic radius)
 - (C) $\text{Li} < \text{B} < \text{Be} < \text{C} < \text{N} < \text{O}$ (2nd ionization energy)
 - (D) $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$ (Ionic mobility)
16. The ionic compound $\text{A}^+ \text{B}^-$ is formed easily when the
 - (A) electron affinity of B is high
 - (B) ionization energy of A is low
 - (C) lattice energy of AB is high
 - (D) lattice energy of AB is low
17. Which of the following is/are correct?
 - (A) For $\text{A}(\text{g}) + \text{e}^- \longrightarrow \text{A}^-(\text{g})$ ΔH may be negative
 - (B) For $\text{A}^-(\text{g}) + \text{e}^- \longrightarrow \text{A}^{2-}(\text{g})$ ΔH may be negative
 - (C) For $\text{A}^-(\text{g}) + \text{e}^- \longrightarrow \text{A}^{2-}(\text{g})$ ΔH must be positive
 - (D) For $\text{Ne}(\text{g}) + \text{e}^- \longrightarrow \text{Ne}^-(\text{g})$ ΔH may be zero

EXERCISE # S-1

- Find out the atomic number of element whose IUPAC name is Unnilpentium.
Fill your answer as sum of digits (excluding decimal places) till you get the single digit answer.
- Select total number of acidic compounds out of given below.
CsOH, OC(OH)₂, SO₂(OH)₂, Sr(OH)₂, Ca(OH)₂, Ba(OH)₂, BrOH, NaOH, O₂NOH
- Total number of enthalpy(s) (out of given eight) of A(g) which is/are **not** associated with conversion of $A_{(g)}^- \longrightarrow A_{(g)}^{+4}$.
IE₁, IE₂, IE₃, IE₄, IE₅, IE₆, EGE₁, EGE₂
(IE = ionization energy, EGE = electron gain enthalpy)
- Write the number of pairs in which size of first element or ion is higher as compared to IInd out of following eight pairs.
(O, S), (He, Ne), (Kr, Ne), (Na, Na⁺), (Cl, Cl⁻), (I⁻, Cl⁻), (Li, Na), (Li⁺, Na⁺)
- Total number of elements which have less IE₁ than that of 'N'.
Be, B, C, F, P, He
- Size of H⁻ is smaller than how many elements among these ?
H, Li, Be, B, C, N, O, F, F⁻
- How many orders are **CORRECT**
(a) Acidic strength \Rightarrow ClOH < BrOH < IOH
(b) Basic strength \Rightarrow MgO < CaO < SrO < BeO
(c) Electronegativity \Rightarrow I < Br < N < O < F
(d) Electron affinity \Rightarrow Mg < Na < Si < S < Cl
(e) % Ionic character \Rightarrow NaF < KF < RbF
- _____ is higher for fluorine as compared to chlorine.
Find the number of properties given below to fill the blank space to make a correct statement.
Atomic mass, Covalent radius, Ionic radius (X⁻), Ionization energy, Electron affinity, Electronegativity, Hydration energy of uninegative ion (X⁻),
- Upto argon find the number of elements which have lower IE₁ as compared to He.
- The number of pairs, in which EA of the second element is more than that of the first element is :
[O, S], [C, N], [O, N], [N, P], [Cl⁺, F⁺], [K⁺, Na⁺]
- For an element the successive ionisation energy values (in eV/atom), are given below.
14.534, 29.601, 47.448, 77.472, 97.888, 552.057, 667.029
Find the number of valence shell electrons in that element.

Subjective :

- Calculate E.N. of chlorine atom on Pauling scale if I.E. of Cl⁻ is 4eV & of E.A. of Cl⁺ is + 13.0 eV.
- Increasing order of ionic size :
N³⁻, Na⁺, F⁻, O²⁻, Mg²⁺

EXERCISE # S-2

Paragraph for Questions 1 to 2

First electron gain enthalpy (in $\frac{\text{kJ}}{\text{mol}}$) of few elements are given below :

Elements	ΔH_{eg}
I	-60
II	-45
III	-328
IV	-295
V	+ 48

Answer the following questions on the basis of above data:

- Which element may be an inert gas
(A) I (B) III (C) IV (D) V
- Which element is most non-metallic among all the elements -
(A) I (B) II (C) III (D) IV

Paragraph for Questions 3 to 4

The IE_1 and the IE_2 in KJ/mol of a few elements designated by U, V, W, X are shown below.

Atom	IE_1	IE_2
U	2464	6110
V	610	7542
W	928	1810
X	1588	3410

Based on the above information answer the following question :-

- Which of the elements represent a noble gas.
(A) U (B) V (C) W (D) X
- Which of the following element belongs to group 1 (IA).
(A) U (B) V (C) W (D) X

Paragraph for Question 5 to 7

Nature of bond can be predicted on the basis of electronegativity of bonded atoms, greater difference in electronegativity (X), more will be the polarity of bond, and polar bond are easily broken in polar solvent like water. For hydroxy acids $X_O - X_A$ difference predict the nature of oxide formed by the element A.

$|X_O - X_A| > |X_O - X_H|$ then A-O-H show basic nature (NaOH)

$|X_O - X_A| < |X_O - X_H|$ then A-O-H show acidic nature (H-O-Cl)

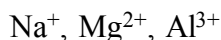
With the help of EN values [$EN_A = 1.8$, $EN_B = 2.6$, $EN_C = 1.6$, $EN_D = 2.8$] answer the following questions for the compounds HAO, HBO, HCO, HDO.

- Compounds whose aqueous solution is acidic and order of their acidic strength
(A) AOH, COH ; AOH < COH (B) HDO, HBO ; HDO > HBO
(C) AOH, COH ; AOH > COH (D) HDO, HBO ; HDO < HBO
- Compounds whose aqueous solution is basic and order of their basic strength
(A) AOH, COH ; AOH < COH (B) HDO, HBO ; HDO > HBO
(C) AOH, COH ; AOH > COH (D) HDO, HBO ; HDO < HBO
- Percentage ionic character of compound AB is
(A) 42.42% (B) 24.24% (C) 15.04% (D) None of these

Paragraph for Question 8 to 12

All the simple salt dissolve in water, producing ions and consequently the solution conduct electricity. In this process water molecule surround both the cations and anions & release energy. This process is called hydration & energy released is called hydration energy & it depends on size of gaseous ions.

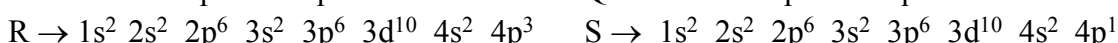
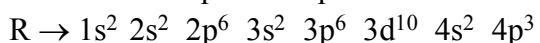
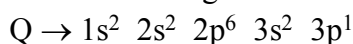
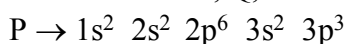
Answer the following questions with respect to given cations.



8. Order of extent of hydration
 (A) $\text{Na}^+ = \text{Mg}^{2+} = \text{Al}^{3+}$ (B) $\text{Na}^+ > \text{Mg}^{2+} > \text{Al}^{3+}$
 (C) $\text{Al}^{3+} > \text{Mg}^{2+} > \text{Na}^+$ (D) $\text{Al}^{3+} > \text{Mg}^{2+} < \text{Na}^+$
9. Order of hydration energy
 (A) $\text{Na}^+ = \text{Mg}^{2+} = \text{Al}^{3+}$ (B) $\text{Na}^+ > \text{Mg}^{2+} > \text{Al}^{3+}$
 (C) $\text{Al}^{3+} > \text{Mg}^{2+} > \text{Na}^+$ (D) $\text{Al}^{3+} > \text{Mg}^{2+} < \text{Na}^+$
10. Order of size of hydrated ion.
 (A) $\text{Na}^+ = \text{Mg}^{2+} = \text{Al}^{3+}$ (B) $\text{Na}^+ > \text{Mg}^{2+} > \text{Al}^{3+}$
 (C) $\text{Al}^{3+} > \text{Mg}^{2+} > \text{Na}^+$ (D) $\text{Al}^{3+} > \text{Mg}^{2+} < \text{Na}^+$
11. Order of ionic mobility
 (A) $\text{Na}^+ = \text{Mg}^{2+} = \text{Al}^{3+}$ (B) $\text{Na}^+ > \text{Mg}^{2+} > \text{Al}^{3+}$
 (C) $\text{Al}^{3+} > \text{Mg}^{2+} > \text{Na}^+$ (D) $\text{Al}^{3+} > \text{Mg}^{2+} < \text{Na}^+$
12. Order of size of gaseous ions.
 (A) $\text{Na}^+ = \text{Mg}^{2+} = \text{Al}^{3+}$ (B) $\text{Na}^+ > \text{Mg}^{2+} > \text{Al}^{3+}$
 (C) $\text{Al}^{3+} > \text{Mg}^{2+} > \text{Na}^+$ (D) $\text{Al}^{3+} > \text{Mg}^{2+} < \text{Na}^+$

Paragraph for Question 13 to 14 are based on the following information.

Four elements P, Q, R & S have ground state electronic configuration as:



13. Comment which of the following option represent the correct order of true (T) & false (F) statement.
 I size of P < size of Q II size of R < size of S
 III size of P < size of R (appreciable difference) IV size of Q < size of S (appreciable difference)
 (A) TTTT (B) TTTF (C) FFTT (D) TTFF
14. Order of IE_1 values among the following is
 (A) $\text{P} > \text{R} > \text{S} > \text{Q}$ (B) $\text{P} < \text{R} < \text{S} < \text{Q}$ (C) $\text{R} > \text{S} > \text{P} > \text{Q}$ (D) $\text{P} > \text{S} > \text{R} > \text{Q}$

Matching List

- | | | |
|-----|---|--|
| 15. | Column-I
Element
(P) Si
(Q) Sc
(R) Ga
(S) Tl | Column-II
Period and group number respectively
(1) 4, 3
(2) 3, 14
(3) 6, 13
(4) 4, 13 |
|-----|---|--|

Code :

- | | | | | |
|-----|----------|----------|----------|----------|
| | P | Q | R | S |
| (A) | 2 | 1 | 3 | 4 |
| (B) | 1 | 2 | 4 | 3 |
| (C) | 2 | 1 | 4 | 3 |
| (D) | 4 | 3 | 1 | 2 |

Match the column

16. Match the column :

Column I

- (A) Highest density
- (B) Metallic character
- (C) Lightest Metal
- (D) Liquid at room temperature

Column II

- (P) Lithium
- (Q) Osmium
- (R) Mercury
- (S) Bromine

17. If electrons are filled in the sub shells of an atom in the following order 1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 4f..... then match the following element in List I with block in List II.

List-I

- (A) K(19)
- (B) Fe(26)
- (C) Ga(31)
- (D) Sn(50)

List-II

- (P) s-Block
- (Q) p-Block
- (R) d-Block
- (S) f-block

18. Match the characteristics mentioned in List II with the process in List I.

List I

- (A) $O(g) + e^- \rightarrow O^-(g)$
- (B) $O^-(g) + e^- \rightarrow O^{2-}(g)$
- (C) $Na^-(g) \rightarrow Na(g) + e^-$
- (D) $Mg^+(g) + e^- \rightarrow Mg(g)$

List II

- (P) Positive electron gain enthalpy
- (Q) Negative electron gain enthalpy
- (R) Exothermic
- (S) Endothermic

19. Match the column :

Column I

- (A) Cl
- (B) F
- (C) Cu
- (D) He

Column II

- (P) Metal
- (Q) Highest negative electron gain enthalpy
- (R) Most Electronegative element
- (S) Highest ionisation energy.

EXERCISE # JEE-MAIN

- According to the Periodic law of elements, the variation in properties of elements is related to their :- [AIEEE-2003]
 - (1) Nuclear masses
 - (2) Atomic numbers
 - (3) Nuclear neutron-proton number ratio
 - (4) Atomic masses
- The atomic numbers of vanadium (V), chromium (Cr), manganese (Mn) and iron (Fe) are respectively 23, 24, 25 and 26. Which one of these may be expected to have the highest second ionization enthalpy? [AIEEE-2003]
 - (1) Cr
 - (2) Mn
 - (3) Fe
 - (4) V
- Among Al_2O_3 , SiO_2 , P_2O_5 and SO_3 , the correct order of acid strength is :- [AIEEE-2004]
 - (1) $\text{Al}_2\text{O}_3 < \text{SiO}_2 < \text{SO}_3 < \text{P}_2\text{O}_5$
 - (2) $\text{SiO}_2 < \text{SO}_3 < \text{Al}_2\text{O}_3 < \text{P}_2\text{O}_5$
 - (3) $\text{SO}_3 < \text{P}_2\text{O}_5 < \text{SiO}_2 < \text{Al}_2\text{O}_3$
 - (4) $\text{Al}_2\text{O}_3 < \text{SiO}_2 < \text{P}_2\text{O}_5 < \text{SO}_3$
- The formation of the oxide ion $\text{O}^{2-}(\text{g})$ requires first an exothermic and then an endothermic step as shown below :- [AIEEE-2004]

$$\text{O}(\text{g}) + \text{e}^- = \text{O}^-(\text{g}), \quad \Delta H^\circ = -142 \text{ kJ mol}^{-1}$$

$$\text{O}^-(\text{g}) + \text{e}^- = \text{O}^{2-}(\text{g}), \quad \Delta H^\circ = 844 \text{ kJ mol}^{-1}$$
 This is because :-
 - (1) O^- ion will tend to resist the addition of another electron
 - (2) Oxygen has high electron affinity
 - (3) Oxygen is more electronegative
 - (4) O^- ion has comparatively larger size than oxygen atom
- In which of the following arrangements, the order is NOT according to the property indicated below? [AIEEE-2005]
 - (1) $\text{Al}^{3+} < \text{Mg}^{2+} < \text{Na}^{1+} < \text{F}^-$ – increasing ionic size
 - (2) $\text{B} < \text{C} < \text{N} < \text{O}$ - increasing first ionization enthalpy
 - (3) $\text{I} < \text{Br} < \text{F} < \text{Cl}$ - increasing electron gain enthalpy (with negative sign)
 - (4) $\text{Li} < \text{Na} < \text{K} < \text{Rb}$ - increasing metallic radius
- Which of the following oxides is amphoteric in character ? [AIEEE-2005]
 - (1) SnO_2
 - (2) SiO_2
 - (3) CO_2
 - (4) CaO
- Which of the following factors may be regarded as the main cause of lanthanide contraction ? [AIEEE-2005]
 - (1) poor shielding of one of 4f electron by another in the subshell
 - (2) effective shielding of one of 4f electrons by another in the subshell
 - (3) poorer shielding of 5d electrons by 4f electrons
 - (4) greater shielding of 5d electrons by 4f electrons
- The increasing order of the first ionization enthalpies of the elements B, P, S and F (lowest first) is:- [AIEEE-2006]
 - (1) $\text{F} < \text{S} < \text{P} < \text{B}$
 - (2) $\text{P} < \text{S} < \text{B} < \text{F}$
 - (3) $\text{B} < \text{P} < \text{S} < \text{F}$
 - (4) $\text{B} < \text{S} < \text{P} < \text{F}$

9. The set representing the correct order of ionic radius is :- [AIEEE-2009]
 (1) $\text{Li}^+ > \text{Na}^+ > \text{Mg}^{2+} > \text{Be}^{2+}$ (2) $\text{Mg}^{2+} > \text{Be}^{2+} > \text{Li}^+ > \text{Na}^+$
 (3) $\text{Li}^+ > \text{Be}^{2+} > \text{Na}^+ > \text{Mg}^{2+}$ (4) $\text{Na}^+ > \text{Li}^+ > \text{Mg}^{2+} > \text{Be}^{2+}$
10. The correct order of electron gain enthalpy with negative sign of F, Cl, Br and I, having atomic number 9, 17, 35 and 53 respectively, is :- [AIEEE-2011]
 (1) $\text{I} > \text{Br} > \text{Cl} > \text{F}$ (2) $\text{F} > \text{Cl} > \text{Br} > \text{I}$ (3) $\text{Cl} > \text{F} > \text{Br} > \text{I}$ (4) $\text{Br} > \text{Cl} > \text{I} > \text{F}$
11. The increasing order of the ionic radii of the given isoelectronic species is :- [AIEEE-2012]
 (1) $\text{K}^+, \text{S}^{2-}, \text{Ca}^{2+}, \text{Cl}^-$ (2) $\text{Cl}^-, \text{Ca}^{2+}, \text{K}^+, \text{S}^{2-}$
 (3) $\text{S}^{2-}, \text{Cl}^-, \text{Ca}^{2+}, \text{K}^+$ (4) $\text{Ca}^{2+}, \text{K}^+, \text{Cl}^-, \text{S}^{2-}$
12. In which of the following arrangements, the sequence is not strictly according to the property written against it ? [JEE-MAIN 2012] (On-Line)
 (1) $\text{CO}_2 < \text{SiO}_2 < \text{SnO}_2 < \text{PbO}_2$: increasing oxidising power
 (2) $\text{B} < \text{C} < \text{O} < \text{N}$: increasing first ionisation enthalpy
 (3) $\text{NH}_3 < \text{PH}_3 < \text{AsH}_3 < \text{SbH}_3$: increasing basic strength
 (4) $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$: increasing acid strength
13. Which of the following represents the correct order of increasing first ionization enthalpy for Ca, Ba, S, Se and Ar ? [JEE-MAIN-2013]
 (1) $\text{Ca} < \text{S} < \text{Ba} < \text{Se} < \text{Ar}$ (2) $\text{S} < \text{Se} < \text{Ca} < \text{Ba} < \text{Ar}$
 (3) $\text{Ba} < \text{Ca} < \text{Se} < \text{S} < \text{Ar}$ (4) $\text{Ca} < \text{Ba} < \text{S} < \text{Se} < \text{Ar}$
14. The first ionisation potential of Na is 5.1 eV. The value of electron gain enthalpy of Na^+ will be :- [JEE-MAIN-2013]
 (1) - 2.55 eV (2) - 5.1 eV (3) - 10.2 eV (4) + 2.55 eV
15. Electron gain enthalpy with negative sign of fluorine is less than that of chlorine due to : [JEE-MAIN 2013 (On-Line)]
 (1) Smaller size of chlorine atom (2) Bigger size of 2p orbital of fluorine
 (3) High ionization enthalpy of fluorine (4) Smaller size of fluorine atom
16. Given [JEE-MAIN 2013 (On-Line)]
- | Reaction | Energy Change (in kJ) |
|---|--------------------------|
| $\text{Li(s)} \longrightarrow \text{Li(g)}$ | 161 |
| $\text{Li(g)} \longrightarrow \text{Li}^+(\text{g})$ | 520 |
| $\frac{1}{2} \text{F}_2(\text{g}) \longrightarrow \text{F(g)}$ | 77 |
| $\text{F(g)} + \text{e}^- \longrightarrow \text{F}^-(\text{g})$ | (Electron gain enthalpy) |
| $\text{Li}^+(\text{g}) + \text{F}^-(\text{g}) \longrightarrow \text{LiF(s)}$ | -1047 |
| $\text{Li(s)} + \frac{1}{2} \text{F}_2(\text{g}) \longrightarrow \text{LiF(s)}$ | -617 |
- Based on data provided, the value of electron gain enthalpy of fluorine would be :
 (1) -300 kJ mol⁻¹ (2) -328 kJ mol⁻¹ (3) -350 kJ mol⁻¹ (4) -228 kJ mol⁻¹

17. The order of increasing sizes of atomic radii among the elements O, S, Se and As is :
[JEE-MAIN 2013 (On-Line)]
- (1) $\text{As} < \text{S} < \text{O} < \text{Se}$ (2) $\text{O} < \text{S} < \text{As} < \text{Se}$
(3) $\text{Se} < \text{S} < \text{As} < \text{O}$ (4) $\text{O} < \text{S} < \text{Se} < \text{As}$
18. Which is the correct order of second ionization potential of C, N, O and F in the following ?
[JEE-MAIN 2013 (On-Line)]
- (1) $\text{O} > \text{F} > \text{N} > \text{C}$ (2) $\text{O} > \text{N} > \text{F} > \text{C}$
(3) $\text{C} > \text{N} > \text{O} > \text{F}$ (4) $\text{F} > \text{O} > \text{N} > \text{C}$
19. Which of the following series correctly represents relations between the elements from X to Y ?
[JEE-MAIN 2014 (On-Line)]
- $\text{X} \longrightarrow \text{Y}$
- (1) $_{18}\text{Ar} \rightarrow _{54}\text{Xe}$ Noble character increases
(2) $_3\text{Li} \rightarrow _{19}\text{K}$ Ionization enthalpy increases
(3) $_6\text{C} \rightarrow _{32}\text{Ge}$ Atomic radii increases
(4) $_9\text{F} \rightarrow _{35}\text{Br}$ Electron gain enthalpy with negative sign increases
20. The ionic radii (in Å) of N^{3-} , O^{2-} and F^- are respectively :- [JEE-MAIN 2015 (Off-Line)]
- (1) 1.71, 1.40 and 1.36 (2) 1.71, 1.36 and 1.40
(3) 1.36, 1.40 and 1.71 (4) 1.36, 1.71 and 1.40
21. In the long form of the periodic table, the valence shell electronic configuration of $5s^2 5p^4$ corresponds to the element present in: [JEE-MAIN 2015 (On-Line)]
- (1) Group 16 and period 5 (2) Group 17 and period 6
(3) Group 17 and period 5 (4) Group 16 and period 6
22. Which of the following atoms has the highest first ionization energy ?
[JEE-MAIN 2016 (Off-Line)]
- (1) Sc (2) Rb (3) Na (4) K
23. The non-metal that does not exhibit positive oxidation state is :
[JEE-MAIN 2016 (On-Line)]
- (1) Oxygen (2) Fluorine (3) Iodine (4) Chlorine
24. The electronic configuration with the highest ionization enthalpy is:- [JEE-MAIN 2017]
- (1) $[\text{Ar}] 3d^{10} 4s^2 4p^3$ (2) $[\text{Ne}] 3s^2 3p^1$
(3) $[\text{Ne}] 3s^2 3p^2$ (4) $[\text{Ne}] 3s^2 3p^3$

25. Consider the following ionization enthalpies of two elements 'A' and 'B' :

Element	Ionization enthalpy (kJ/mol)		
	1 st	2 nd	3 rd
A	899	1757	14847
B	737	1450	7731

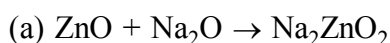
[JEE-MAIN 2017]

Which of the following statements is correct ?

- (1) Both A and B belong to group-2 where A comes below B
- (2) Both A and B belong to group-1 where A comes below B
- (3) Both A and B belong to group-1 where B comes below A
- (4) Both A and B belong to group-2 where B comes below A

26. In the following reactions, ZnO is respectively acting as a/an :

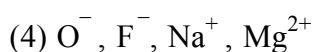
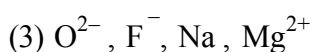
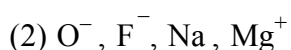
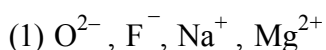
[JEE-MAIN 2017]



- (1) base and acid (2) base and base (3) acid and acid (4) acid and base

27. The group having isoelectronic species is :-

[JEE-MAIN 2017]



EXERCISE # JEE-ADVANCED

1. **Statement-1** : F atom has a less negative electron gain enthalpy than Cl atom. [JEE 2000]
Statement-2 : Additional electron is repelled more efficiently by 3p electron in Cl atom than by 2p electron in F atom.
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
 (C) Statement-1 is true, statement-2 is false.
 (D) Statement-1 is false, statement-2 is true.
2. The correct order of radii is: [JEE 2000]
 (A) $N < Be < B$ (B) $F^- < O^{2-} < N^{3-}$ (C) $Na < Li < K$ (D) $Fe^{3+} < Fe^{2+} < Fe^{4+}$
3. The IE_1 of Be is greater than that of B. [T/F] [JEE 2001]
4. The set representing correct order of IP_1 is [JEE 2001]
 (A) $K > Na > Li$ (B) $Be > Mg > Ca$ (C) $B > C > N$ (D) $Fe > Si > C$
5. Identify the least stable ion amongst the following: [JEE 2002]
 (A) Li^- (B) Be^- (C) B^- (D) C^-
6. The increasing order of atomic radii of the following group 13 elements is [JEE 2016]
 (A) $Al < Ga < In < Tl$ (B) $Ga < Al < In < Tl$
 (C) $Al < In < Ga < Tl$ (D) $Al < Ga < Tl < In$
7. The option(s) with only amphoteric oxides is (are): [JEE 2017]
 (A) Cr_2O_3 , CrO , SnO , PbO
 (B) NO , B_2O_3 , PbO , SnO_2
 (C) Cr_2O_3 , BeO , SnO , SnO_2
 (D) ZnO , Al_2O_3 , PbO , PbO_2

ANSWERS KEY

EXERCISE # O-1

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	D	A	A	D	A	B	C	A	C	A
Que.	11	12	13	14	15	16	17	18	19	20
Ans.	C	B	A	B	C	C	B	C	B	C
Que.	21	22	23	24	25	26	27	28	29	30
Ans.	B	C	C	B	A	C	A	C	A	B
Que.	31	32	33	34	35	36	37	38	39	40
Ans.	D	B	B	D	C	C	D	C	D	B
Que.	41	42	43	44	45	46	47	48	49	
Ans.	C	B	B	A	A	C	A	D	D	

EXERCISE # O-2

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	A,B,C,D	A, B, D	A, C	B, C	A, B, C	A, B	B, D	A, B	B, C	A,B,C,D
Que.	11	12	13	14	15	16	17			
Ans.	A, B, D	A, B	A, C, D	B, C, D	A, B, D	A, B, C	A, C			

EXERCISE # S-1

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	6	4	3	3	4	0	3	3	17	4
Que.	11	12	13							
Ans.	5	3.03 (Pauling)	$Mg^{2+} < Na^{+} < F^{-} < O^{2-} < N^{3-}$							

EXERCISE # S-2

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	D	C	A	B	B	A	C	C	C	C
Que.	11	12	13	14	15	16				
Ans.	B	B	B	A	C	(A)→Q;(B)→P,Q,R ;(C)→P;(D)→R, S				
Que.	17					18				
Ans.	(A)→R ; (B)→R ; (C)→Q ; (D)→S					(A) → Q,R ; (B) → P,S ; (C) → S ; (D) → Q,R				
Que.	19									
Ans.	(A) → Q ; (B) → R ; (C) → P ; (D) → S									

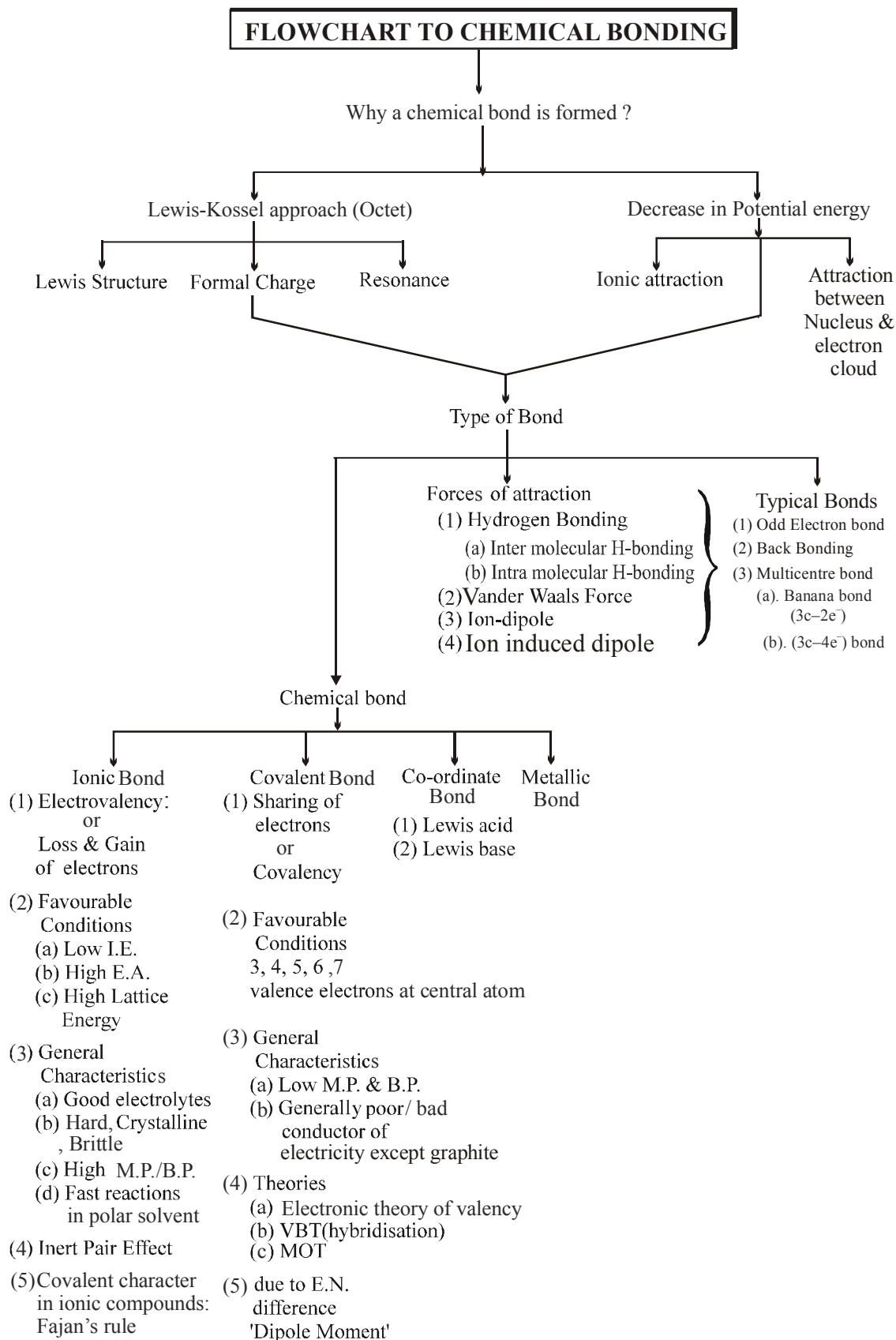
EXERCISE # JEE-MAIN

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	2	1	4	1	2	1	3	4	4	3
Que.	11	12	13	14	15	16	17	18	19	20
Ans.	4	3	3	2	4	2	4	1	3	1
Que.	21	22	23	24	25	26	27			
Ans.	1	1	2	4	4	4	1			

EXERCISE # JEE-ADVANCED

Que.	1	2	3	4	5	6	7			
Ans.	C	B	T	B	B	B	C, D			

CHEMICAL BONDING



KEY CONCEPT

CHEMICAL BOND

- The attractive force which holds various constituents (atoms, ions, etc.) together in different chemical species is called a chemical bond.
- It is the combination of two or more chemical species involving redistribution of e^- among them.
- This process is accompanied with decrease in energy.
- Decrease in energy strengthens the bond.
- Therefore, molecules are more stable than atoms.

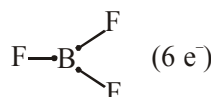
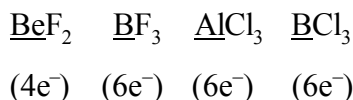
CAUSE OF CHEMICAL COMBINATION

- Tendency to acquire minimum energy :**
- Tendency to acquire noble gas configuration (Octet rule) :**

Atoms combine to complete an octet of electrons in their outer most shell. Hence all atoms have a tendency to acquire octet (ns^2np^6) configuration or to attain nearest noble gas configuration in their outermost orbit. This can be achieved by combining with other atom or ion.

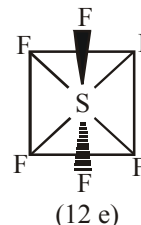
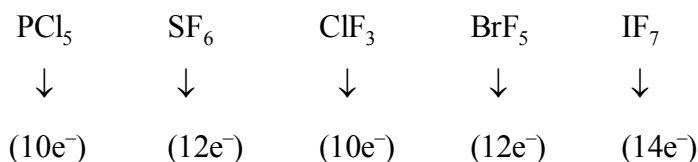
LIMITATION OF OCTET RULE

- Contraction of octet (incomplete octet)**



These compounds are hypovalent.

- Expansion of Octet (due to empty d-orbitals)**



These compounds are hypervalent.

- Odd electron species**

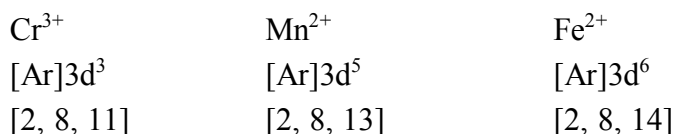
Ex. NO, NO₂, ClO₂ etc.

OTHER EXCEPTIONS OF OCTET RULE

- Compounds of Noble gases**

Noble gases which have already completed their octets (or duplet in case of He.) should not form compounds. However, their compounds like XeF₂, XeF₆ & KrF₂ etc., have been actually prepared.

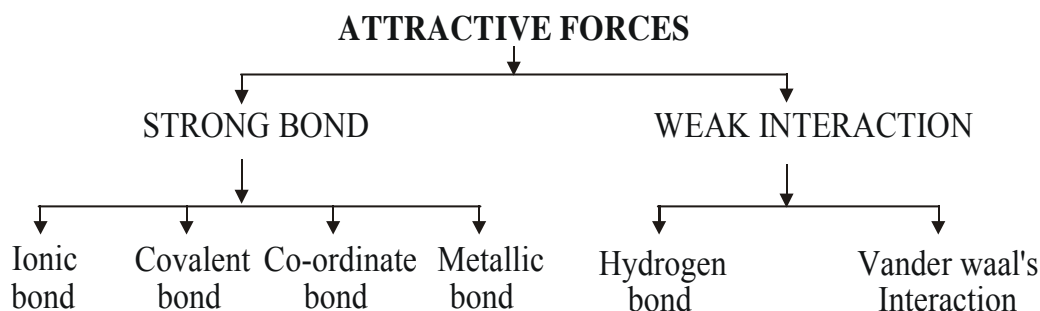
- Transition metal ions**



- Pseudo inert gas configuration $[(n-1)d^{10}ns^2np^6]$**



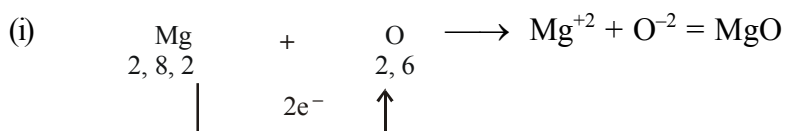
CLASSIFICATION OF BONDS



ELECTROVALENT OR IONIC BOND

- (a) The chemical bond formed between two or more atoms as a result of the complete transfer of one or more electrons from one atom to another is called as Ionic or electrovalent bond.

Example



electrovalency of Mg = 2

electrovalency of O = 2

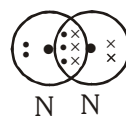
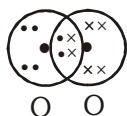
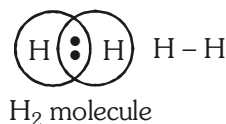
Note : Ionic bond is non-directional.

FACTORS FAVOURING IONIC BONDING

- Less Ionization energy of atom forming cation
- Higher electron affinity of atom forming anion
- Greater Lattice energy of formed product.
- Greater Electronegativity difference between atoms forming cation & anion.

COVALENT BOND

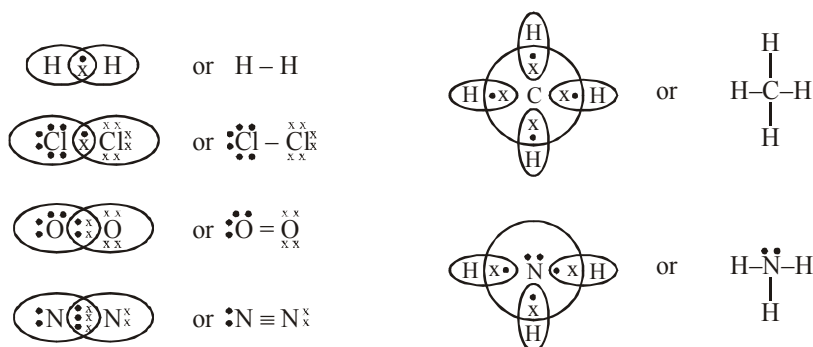
- (a) A covalent bond is formed by the mutual sharing of electrons between two atoms.



- The shared pair of electrons must have opposite spins, and are localised between two atoms concerned.
- On the basis of electrons being shared between two atoms the bonds are of three types –

Covalency : Capacity to form covalent bond is known as covalency

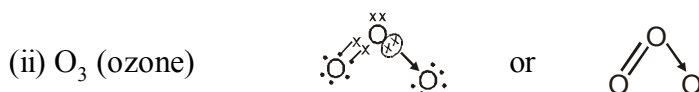
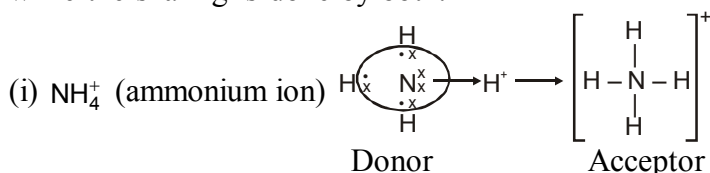
It is represented by (–) small line. – means single bond ; = means double bond ; \equiv means triple bond.



★ Covalent bonds are directional in nature

COORDINATE BOND (DATIVE BOND)

The bond formed between two atom in which contribution of an electron pair is made by one of them while the sharing is done by both.

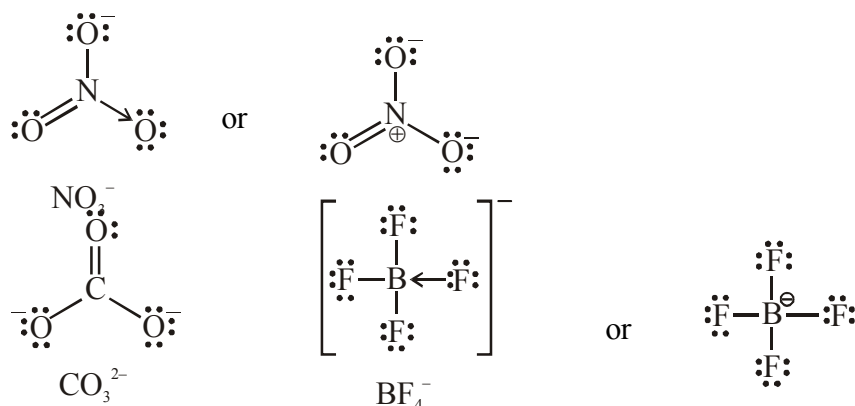


Lewis Dot structures:

- ★ Arrangement of various atoms in a molecule & types of bonding present in it but no idea of geometry of the molecule.
- ★ In most cases we can construct a Lewis structure in three steps :
 - (1) Decide on the number of electrons that are included in the structure by adding together the number of all the valence electrons provided by the atoms.
 - (2) Write the chemical symbols of the atoms in the arrangement that shows which atoms are bonded together.
 - (3) Distribute the electrons in pairs so that there is one pair of electrons forming a single bond between each pair of atom bonded together and then supply electron pairs (to form lone pairs or multiple bonds) until each atom has an octet.
- ★ In oxy acids all 'H' atoms are attached to oxygen as $-\text{OH}$ groups except in H_3PO_3 (dibasic), H_3PO_2 (monobasic) & $\text{H}_4\text{P}_2\text{O}_5$ (dibasic). Which are directly bonded to central atom.

Applications :

- ★ To know various linkages present
- ★ To calculate formal charge of various elements.



FORMAL CHARGE

Lewis dot structures, in general, do not represent the actual shapes of the molecules. In case of polyatomic ions, the net charge is possessed by the ion as a whole and not by a particular atom. It is, however, feasible to assign a formal charge on each atom.

$$\text{Formal Charge : } Q_F = N_A - N_{L.P.} - \frac{1}{2} N_{B.P.}$$

Where :

N_A = Total number of valence electron in the free atom

$N_{L.P.}$ = Total number of non bonding (lone pair) electrons

$N_{B.P.}$ = Total number of bonding (shared) electrons

Molecule	Structure	Formal Charge
O_3		$O(1) = 6 - 2 - \frac{1}{2} (6) = +1$ $O(2) = 6 - 4 - \frac{1}{2} (4) = 0$ $O(3) = 6 - 6 - \frac{1}{2} (2) = -1$
CO		$C = 4 - 2 - \frac{1}{2} \times 6 = -1$ $O = 6 - 2 - \frac{1}{2} \times 6 = +1$
NH_4^+		$N = 5 - 0 - \frac{1}{2} (8) = +1$ $\text{On each H} = 1 - 0 - \frac{1}{2} (2) = 0$

RESONANCE*

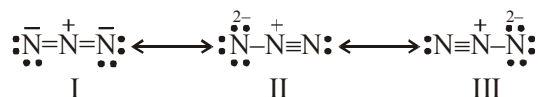
When a molecule cannot be completely represented by a single Lewis structure but its characteristic properties can be described by two or more different structures, with similar energy position of nuclei, bonding and non-bonding pairs of electrons, then the true structure is said to be resonance hybrid of these structures. The phenomenon is called resonance and different contributing structures are called resonating structures or canonical structures.

- ❖ Resonance stabilizes the molecule as the energy of the resonance hybrid is less than the energy of any single canonical structure.
- ❖ Resonance averages the bond characteristics as a whole.
- ❖ The canonical forms have no real existence.

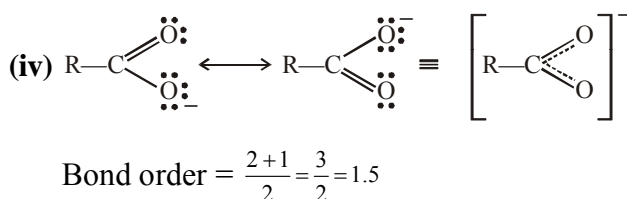
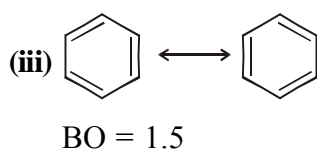
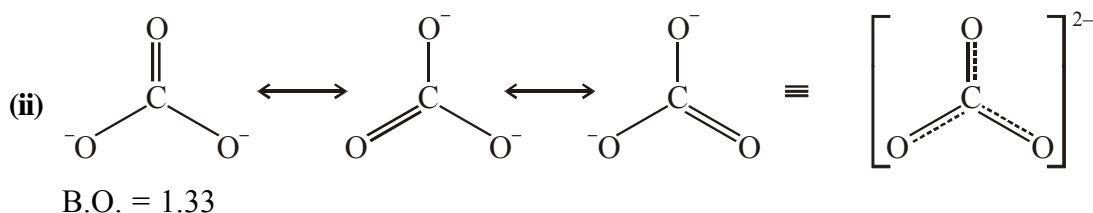
Resonance Structure of Some Molecules/Ions :

(i) Azide ion, N_3^- :

The azide ion may be represented as -



The structures II and III contribute equally and the molecule has almost double bond character in each N-N bond.



*Descriptive discussion of concept of resonance will be done in **Organic Chemistry**.

VALENCE BOND THEORY

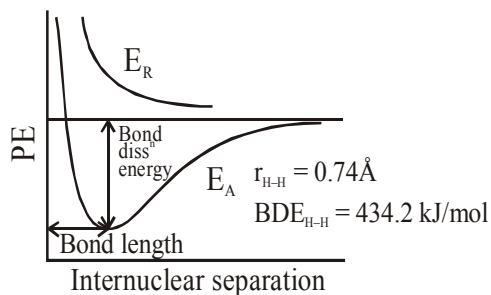
Valence bond theory was introduced by Heitler and London (1927) and developed further by Pauling and others. A discussion of the valence bond theory is based on the knowledge of atomic orbitals, electronic configurations of elements, the overlap criteria of atomic orbitals and the hybridization of atomic orbitals.

Formation of H_2 molecule :

When two 'H'-atoms approaches towards each other for the formation of H_2 molecule. The following interactions takes place.

- (i) e-e repulsion
- (ii) e-p attraction
- (iii) p-p repulsion

Experimentally, it has been found that the magnitude of attractive forces is more than the repulsive forces. As a result, when two atoms approach each other then potential energy decreases. Ultimately a stage is reached where the net force of attraction balances the force of repulsion and system acquires minimum energy.



The potential energy curve for the formation of H_2 molecule as a function of internuclear distance of the H atoms. The minimum in the curve corresponds to the most stable state of H_2 .

At this stage two hydrogen atoms are said to be bonded together to form a stable molecule having the bond length of 74 pm. Since the energy gets released when the bond is formed between two hydrogen atoms, the hydrogen molecule is more stable than that of isolated hydrogen atoms.

Bond Length : Internuclear distance at minimum potential energy is called bond length.

Bond Dissociation Energy : The amount of energy released when one mole of same type of bonds are formed is called B.D.E.

434.2 kJ/mol of energy is required to dissociate one mole of H_2 molecule.



ORBITAL OVERLAP CONCEPT

In the formation of hydrogen molecule, there is a minimum energy state when two hydrogen atoms are so near that their atomic orbitals undergo partial interpenetration. This partial merging of atomic orbitals is called overlapping of atomic orbitals which results in the pairing of electrons. The extent of overlap decides the strength of a covalent bond. In general, greater the overlap the stronger is the bond formed between two atoms. Therefore, according to orbital overlap concept, the formation of a covalent bond between two atoms results by pairing of electrons, present in the valence shell having opposite spins.

Directional Properties of Bonds :

The valence bond theory explains the formation and directional properties of bonds in polyatomic molecules like CH_4 , NH_3 and H_2O , etc. in terms of overlap and hybridisation of atomic orbitals.

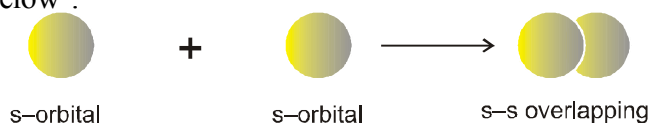
Types of Overlapping and Nature of Covalent Bonds

The covalent bond may be classified into following types depending upon the types of overlapping :-

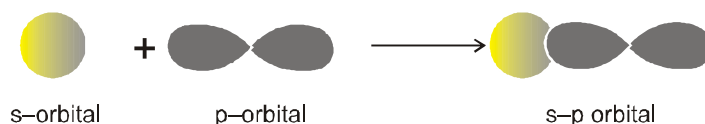
(i) sigma(σ) bond (ii) pi(π) bond (iii) delta(δ) bond

- (i) **Sigma (σ) bond :** This type of covalent bond is formed by the end to end (head on or axial) overlap of bonding orbitals along the internuclear axis. This can be formed by any one of the following types of combinations of atomic orbitals.

- s-s overlapping : In this case, there is overlap of two half filled s-orbitals along the internuclear axis as shown below :



- s-p overlapping: This type of overlap occurs between half filled s-orbital of one atom and half filled p-orbital of another atom.

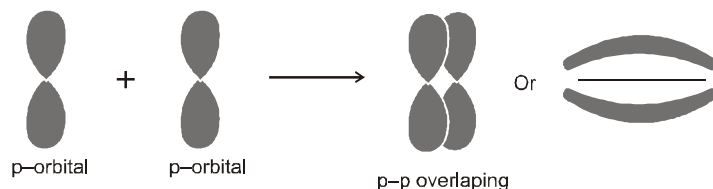


- p-p overlapping : This type of overlap takes place between half filled similar p-orbitals of the two approaching atoms.

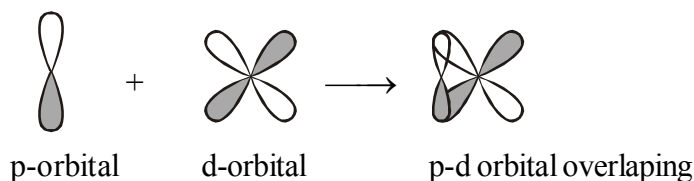


- (ii) **pi(π) bond** : In the formation of π bond the atomic orbitals overlap in such a way that their axis remain parallel to each other and perpendicular to the internuclear axis. The orbitals formed due to sidewise overlapping consists of two saucer type charged clouds above and below the plane of the participating atoms.

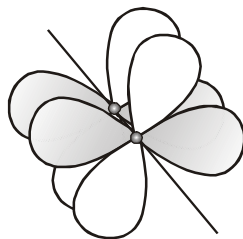
(a) **$p_{\pi}-p_{\pi}$**



(b) **$p_{\pi}-d_{\pi}$**



- (iii) **delta (δ) bond** : are the covalent bonds where four lobes of d-orbital of one atom overlap with four lobes of the similar d-orbital of other atom. Except d_{z^2} all d orbitals form δ bond.



Strength of sigma and pi Bonds :

Basically the strength of a bond depends upon the extent of overlapping- In case of sigma bond, the overlapping of orbitals takes place to a larger extent. Hence, it is stronger as compared to the pi bond where the extent of overlapping occurs to a smaller extent. Further, it is important to note that pi bond between two atoms is formed in addition to a sigma bond. It is always present in the molecules containing multiple bond (double or triple bonds)

Advantages of VBT :

- ❖ It explain various bond characteristics e.g., bond length, bond strength.
- ❖ It explains the quantitative relationship between the extent of overlapping and bond dissociation energy.
- ❖ This theory accounts for shape and nature of bonding of the molecule whose covalency is not according to the number of half-filled orbitals present in the ground state.
- ❖ This theory redefined the stability of molecules e.g. BF_3 , AlCl_3 , PCl_5 , SF_6 etc which are exception to octet rule.

Disadvantages of VBT :

- ❖ According to this theory three bond angle in CH_4 should be 90° , as these are formed by p-p overlapping, but actually it has four $109^\circ 28'$ angles. In NH_3 & H_2O , angle should be 90° . This is in disagreement with the actual bond angles of 107° & 104.5° in NH_3 & H_2O molecules respectively.
- ❖ In order to explain the characteristic geometrical shapes of polyatomic molecules like CH_4 , NH_3 , H_2O etc. Pauling introduced the concept of hybridisation.

HYBRIDISATION

The phenomenon of intermixing of the orbitals of slightly different energies so as to redistribute their energies, resulting in the formation of new set of orbitals of equivalent energies and shape. For example when one 2s and three 2p-orbitals of carbon hybridise, there is the formation of four new sp^3 hybrid orbitals.

Salient features of hybridisation: The main features of hybridisation are as under :

1. The number of hybrid orbitals is equal to the number of the atomic orbitals that get hybridised.
2. The hybridised orbitals are always equivalent in energy and shape.
3. The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.
4. These hybrid orbitals are directed in space in some preferred direction to have minimum repulsion between electron pairs and thus a stable arrangement. Therefore, the type of hybridisation indicates the geometry of the molecules.

Important conditions for hybridisation

- (i) The orbitals present in the valence shell of the atom are hybridised.
- (ii) The orbitals undergoing hybridisation should have almost equal energy.
- (iii) Promotion of electron is not essential condition prior to hybridisation.
- (iv) It is not necessary that only half filled orbitals participate in hybridisation. In some cases, even filled orbitals of valence shell take part in hybridisation.

Types of Hybridisation

There are various types of hybridisation involving s, p and d orbitals. The different types of hybridisation are as under :

- (i) sp hybridisation (ii) sp^2 hybridisation (iii) sp^3 hybridisation
 (iv) sp^3d hybridisation: (v) sp^3d^2 hybridisation: (vi) sp^3d^3 hybridisation:

Determination of hybridisation state –

To predict hybridisation following formula may be used :

Number of hybrid orbital = Steric Number (S.N.) = Number of σ -bond around that atom + Number of lone pair on that atom.

Molecule	Method	Hybridisation
NH_4^+	$S.N. = 4 + 0 = 4$	sp^3 hybridisation.

Number of hybrid orbitals	Hybridisation
two	sp
three	sp^2
four	sp^3
five	sp^3d
six	sp^3d^2
seven	sp^3d^3

Hybridisation in Ionic solid species :


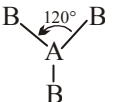
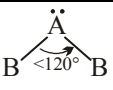
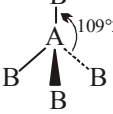
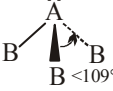
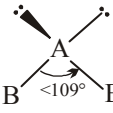
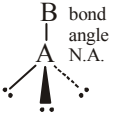
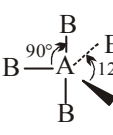
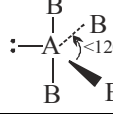
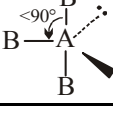
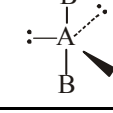
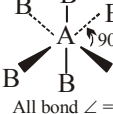
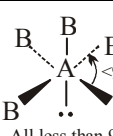
Species	Cationic part	Anionic part
PCl_5	$\text{PCl}_4^+ (\text{sp}^3)$	$\text{PCl}_6^- (\text{sp}^3\text{d}^2)$
PBr_5	$\text{PBr}_4^+ (\text{sp}^3)$	Br^-
XeF_6	$\text{XeF}_5^+ (\text{sp}^3\text{d}^2)$	F^-
N_2O_5	$\text{NO}_2^+ (\text{sp})$	$\text{NO}_3^- (\text{sp}^2)$
I_2Cl_6 (liquid)	$\text{ICl}_2^+ (\text{sp}^3)$	$\text{ICl}_4^- (\text{sp}^3\text{d}^2)$
Cl_2O_6	$\text{ClO}_2^+ (\text{sp}^2)$	$\text{ClO}_4^- (\text{sp}^3)$

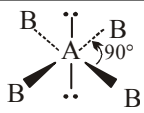
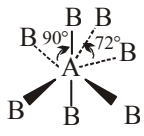
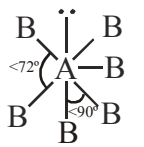
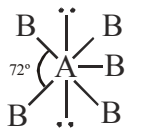
VALENCE SHELL ELECTRON PAIR REPULSION THEORY (VSEPR)

- (a) Molecules having covalent bond have definite geometry as covalent bonding has directional characteristics. A simple theory was given for the molecular shape of the covalent molecules by Gillespie and Nyholm in 1957.
- (b) This theory predicts the shape of the molecule by considering the most stable configuration of the bond angles in the molecule. This theory states
 - (i) Electron pairs in the valence shell of the central atom of a molecule, whether bonding or lone pairs are regarded as occupying localised orbitals. These orbitals arrange themselves in so as to minimize the mutual electronic repulsions.
 - (ii) The magnitude of the different types of electronic repulsions follows the order given below:

lone pair-lone pair > lone pair - bonded pair > bonded pair - bonded pair
 - (iii) The electronic repulsion between two pairs of electrons will be minimum if they are as far apart as possible.
 - (iv) The actual shape of the molecules containing lone pairs is a little distorted from the basic shape as in the NH_3 and H_2O molecules, the bond angles are not $109^\circ 28'$ but 107° and 104.5° respectively due to presence of one lone pair in NH_3 and two lone pairs in H_2O .

SHAPES OF MOLECULES BASED ON VSEPR THEORY

Total no. of hybrid orbitals	No. of b.p. (bond pairs)	No. of unshared pair i.e. l_p	General formula	Type of hybridisation	Stereo chemical formula/str.	Shape	Exam.
2	2	0	AB_2	sp		linear	$BeCl_2$
3	3	0	AB_3	sp^2		Trigonal planar	BCl_3 , NO_3^- , GaF_3 , CO_3^{2-}
3	2	1	AB_2	sp^2		V or Bent or angular	$SnCl_2$, O_3 , SO_2
4	4	0	AB_4	sp^3		Tetrahedron	CH_4 , SiF_4 , NH_4^+
4	3	1	AB_3	sp^3		Trigonal pyramidal	NH_3 , CH_3^-
4	2	2	AB_2	sp^3		V or Bent or angular	H_2O , SF_2
4	1	3	AB	sp^3		linear	ClO^-
5	5	0	AB_5	sp^3d		Trigonal bipyramidal	PF_5 , SF_5^+ , $SbBr_5$, XeO_3F_2
5	4	1	AB_4	sp^3d		Seesaw	SF_4
5	3	2	AB_3	sp^3d		T-shaped	ClF_3 , BrF_3
5	2	3	AB_2	sp^3d		Linear	ICl_2^- , XeF_2 , I_3^-
6	6	0	AB_6	sp^3d^2		Octahedral or Square bipyramidal	SF_6 , IF_6^+
6	5	1	AB_5	sp^3d^2		Square pyramidal	IF_5 , $XeOF_4$, BrF_5

6	4	2	AB_4	sp^3d^2		Square planar	IF_4^- , XeF_4 , ICl_4
7	7	0	AB_7	sp^3d^3		Pentagonal bipyramidal	IF_7
7	6	1	AB_6	sp^3d^3		Distorted octahedral	XeF_6 , IF_6^-
7	5	2	AB_5	sp^3d^3		Pentagonal planar	XeF_5^-

BOND PARAMETERS

(I) Bond order

(II) Bond Length (Bond distance)

(III) Bond Angle

(IV) Bond Enthalpy

(I) Bond order :

The Bond Order is given by the number of bonds between the two atoms in a molecule.

The bond order, for example in H_2 (with a single shared electron pair), in O_2 (with two shared electron pairs) and in N_2 (with three shared electron pairs) is 1,2,3 respectively.

Note : Isoelectronic molecules and ions have identical bond orders; for example, F_2 and O_2^{2-} have bond order 1. N_2 , CO and NO^+ have bond order 3.

Note : A general correlation useful for understanding the stabilities of molecules is that: with increase in bond order, bond enthalpy increases and bond length decreases.

(II) Bond Length :-

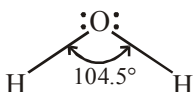
Bond length is defined as the equilibrium distance between the nuclei of two bonded atoms in a molecule. Bond lengths are measured by spectroscopic, X-ray diffraction and electron-diffraction techniques about which you will learn in higher classes.

Factors affecting bond length

- | | |
|-----------------------------|---|
| (a) Size of atoms | (b) Effect of bond order or number of bonds |
| (c) Effect of Resonance | (d) Effect of Electronegativity difference |
| (f) Effect of Hybridisation | |

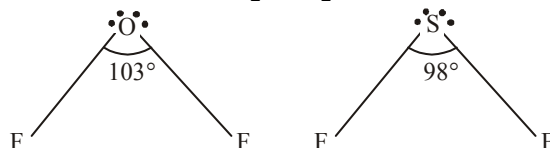
(III) Bond angle :

It is defined as the angle between the orbitals containing bonding electron pairs around the central atom in a molecule/complex ion. Bond angle is expressed in degree which can be experimentally determined by spectroscopic methods. For example $H-\hat{O}-H$ bond angle in water can be represented as under :



Comparison of bond angles.

- (a) If central atoms are in different hybridisations then it can be compared.
 (b) If same hybridisation but different central atoms then bond angle would be more of the molecule in which central atom is more E.N. eg. OF_2 , SF_2



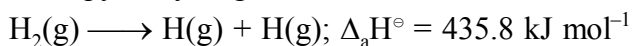
- (c) Molecules having same C.A. but different substituent then bond angle increases as the size of attached atom increases except in symmetrical molecules and H_2O / F_2O , NH_3 / NF_3

Factors affecting bond angle

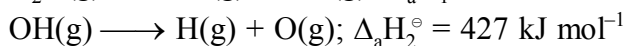
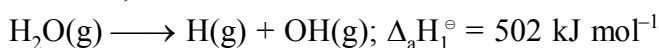
- State of Hybridisation
- Presence of lone pair
- Electronegativity of central atom
- Electronegativity of surrounding atom
- Size of surrounding atom
- Lone pairs may sometimes be transferred from a filled shell of one atom to an unfilled shell of another bonded atom, causing less repulsion.
- Multiple bond orbital repel other orbitals more strongly than single bond orbitals.

(IV) Bond Enthalpy

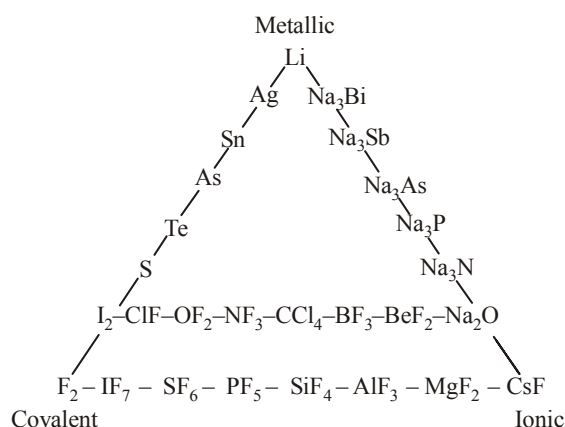
It is defined as the amount of energy required to break one mole of bonds of a particular type between two atoms in a gaseous state. The unit of bond enthalpy is kJ mol^{-1} . For example, the H – H bond enthalpy in hydrogen molecule is $435.8 \text{ kJ mol}^{-1}$.



⇒ In polyatomic molecules the **term mean or average bond enthalpy** is used. It is obtained by dividing total bond dissociation enthalpy by the number of bonds broken as explained below in case of water molecule,

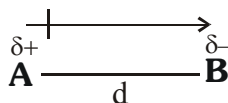


$$\text{Average bond enthalpy} = \frac{502 + 427}{2} = 464.5 \text{ kJ mol}^{-1}$$

SUMMARY OF THE THREE MAIN TYPES OF BONDS

DIPOLE MOMENT

- The degree of polarity of covalent bond is given by the dipole moment (μ)
- It is the product of the either charge and the distance between them.



Electronegativity of A < Electronegativity of B

$$\mu = \delta \times d$$

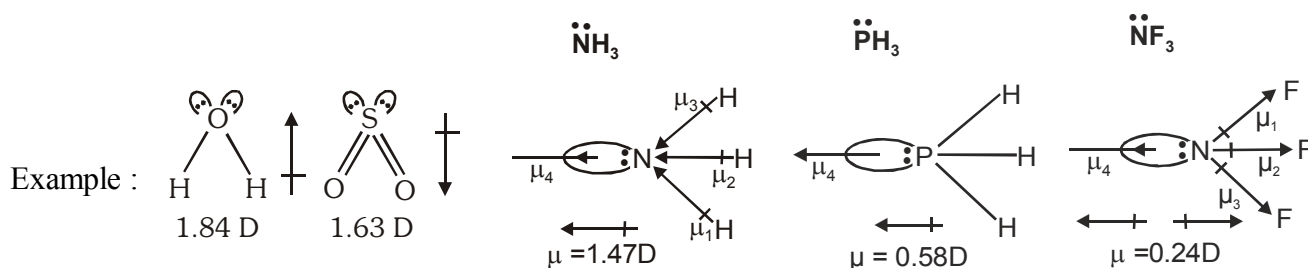
- Dipole moment is a vector quantity.
The direction of dipole moment is represented by \rightarrow
- Units = Cm (S.I.) or esu cm (CGS) or Debye (common unit)
- 1 D = 10^{-18} esu cm = 3.33×10^{-30} coulomb m

Dipole moment depends on

- Electronegativity difference between bonded atoms
- Direction of bond dipole moment
- Angle between various bonds
- Influence of unshared e^- pairs
- Magnitude of polarity of the molecule
- Symmetrical / Unsymmetrical shape.

Application of dipole moment

- To determine the polarity and geometry of molecules



- To calculate the percentage of ionic character

$$\% \text{ ionic character} = \frac{\text{observed } \mu}{\text{calculated } \mu \text{ (for 100 \% ionic)}} \times 100 \%$$

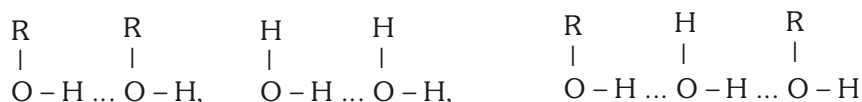
HYDROGEN BONDING

- ★ **Hydrogen bonding:** When a hydrogen atom is bonded to a highly electronegative atom (like F, O or N) comes under the influence of another strongly electronegative atom, then a weak electrostatic force of attraction is developed between them, which is called as hydrogen bond.

Types of H-bonding:

- ★ Intermolecular H-bond

(i) This type of H-bonding takes place between two molecules. **Ex.** ROH, H₂O, R - OH & H₂O

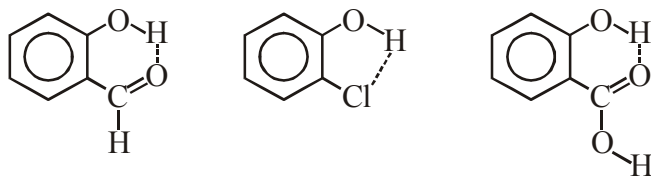


(ii) In such compounds molecular wt., M.P. & B.P. are high.

(iii) Extent of Inter molecular H-bonding \uparrow viscosity & density \uparrow .

- ★ Intramolecular H-bond

Normally when 2 hydroxyl groups are present on the same carbon atom i.e. gem diols are unstable, but "chloralhydrate" is a stable molecule due to formation of H-bond.



Properties influenced by hydrogen bonding

- Abnormal behaviour of water.
- Association of molecules eg. dimerisation of CH₃COOH, HCOOH
- Dissociation of a polar species.
- Abnormal melting point & boiling point.
- Enhanced solubility in water.

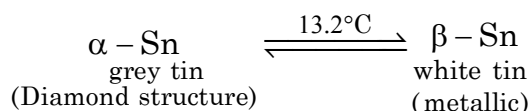
★ **Metallic bonds :**

Electron gas model or sea model, with metal atom existing as kernels along with less firmly held valence electrons & bonds between various kernels (at the lattice site) & valence electrons are known as metallic bonds.

ALLOTROPE OF CARBON FAMILY

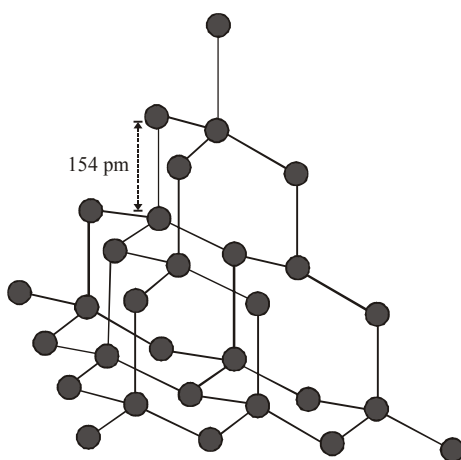
Carbon exhibits many allotropic forms; both crystalline as well as amorphous. Diamond and graphite are two well-known crystalline forms of carbon. In 1985, third form of carbon known as **fullerenes** was discovered by H.W.Kroto, E.Smalley and R.F.Curl. For this discovery they were awarded the Nobel Prize in 1996.

Si, Ge and Sn have a diamond type of structure, though Sn exists as a metallic form. Pb exists only in the metallic form. Ge is unusual because the liquid expands when it forms the solid. This property is unique to Ga, Ge and Bi.



Diamond (*kinetically most stable allotrope of carbon, meta stable phase of carbon*)

It has a crystalline lattice. In diamond each carbon atom undergoes sp^3 hybridisation and linked to four other carbon atoms by using hybridised orbitals in tetrahedral fashion. The C—C bond length is 154 pm. The structure extends in space and produces a rigid three dimensional network of carbon atoms.



The structure of diamond

In this structure, directional covalent bonds are present throughout the lattice. It is very difficult to break extended covalent bonding and, therefore, diamond is a very hard substance. It is used as an abrasive for sharpening hard tools, in making dyes and in the manufacture of tungsten filaments for electric light bulbs.

Problem

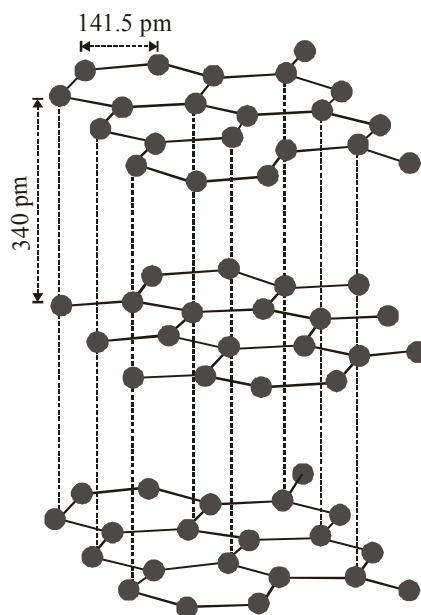
Diamond is covalent, yet it has high melting point. Why ?

Solution

Diamond has a three-dimensional network involving strong C—C bonds, which are very difficult to break and, in turn has high melting point.

Graphite (*Thermodynamically most stable allotrope of carbon*)

Graphite has layered structure. Layers are held by van der Waals forces and distance between two layers is 340 pm. Each layer is composed of planar hexagonal rings of carbon atoms. C—C bond length within the layer is 141.5 pm. Each carbon atom in hexagonal ring undergoes sp^2 hybridisation and makes three sigma bonds with three neighbouring carbon atoms. Fourth electron forms a π bond. The electrons are delocalised over the whole sheet. Thus, graphite is lustrous. Electrons are mobile and,



The structure of graphite

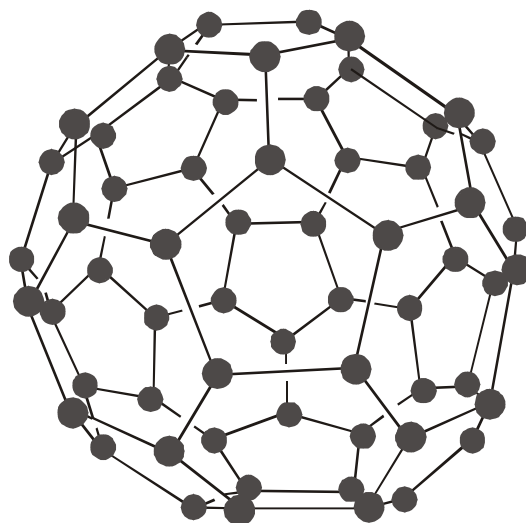
therefore, graphite conducts electricity along the sheet. Graphite cleaves easily between the layers and, therefore, it is very soft and slippery. For this reason graphite is used as a dry lubricant in machines running at high temperature, where oil cannot be used as a lubricant.

Fullerenes

Fullerenes are made by the heating of graphite in an electric arc in the presence of inert gases such as helium or argon. The sooty material formed by condensation of vapourised C_n small molecules consists of mainly C_{60} with smaller quantity of C_{70} and traces of fullerenes consisting of even number of carbon atoms up to 350 or above. Fullerenes are the only pure form of carbon because they have smooth structure without having 'dangling' bonds. Fullerenes are cage like molecules. C_{60} molecule has a shape like soccer ball and called **Buckminsterfullerene**.

It contains twenty, six-membered rings and twelve, five membered rings. A six membered ring is fused with six or five membered rings but a five membered ring can only fuse with six membered rings. All the carbon atoms are equal and they undergo sp^2 hybridisation. Each carbon atom forms three sigma bonds with other three carbon atoms. The remaining electron at each carbon is delocalised in molecular orbitals, which in turn give aromatic character to molecule. However, because of non-planar nature of fullerenes, their aromatic character gets diminished and reactivity increases.

This ball shaped molecule has 60 vertices and each one is occupied by one carbon atom and it also contains both single and double bonds with C–C distances of 143.5 pm and 138.3 pm respectively. Spherical fullerenes are also called *bucky balls* in short.



[The structure of C_{60} , Buckminsterfullerene : Note that molecule has the shape of a soccer ball (football)]

It is very important to know that graphite is thermodynamically most stable allotrope of carbon and, therefore, ΔH_f of graphite is taken as zero. ΔH_f values of diamond and fullerene, C_{60} are 1.90 and 38.1 kJ mol⁻¹, respectively.

Other forms of elemental carbon like carbon black, coke, and charcoal are all impure forms of graphite or fullerenes. Carbon black is obtained by burning hydrocarbons in a limited supply of air. Charcoal and coke are obtained by heating wood or coal respectively at high temperatures in the absence of air.

Uses of Carbon

Graphite fibres embedded in plastic material form high strength, lightweight composites. The composites are used in products such as tennis rackets, fishing rods, aircrafts and canoes. Being good conductor, graphite is used for electrodes in batteries and industrial electrolysis. Crucibles made from graphite are inert to dilute acids and alkalies. Being highly porous, activated charcoal is used in adsorbing poisonous gases; also used in water filters to remove organic contaminants and in airconditioning system to control odour. Carbon black is used as black pigment in black ink and as filler in automobile tyres. Coke is used as a fuel and largely as a reducing agent in metallurgy. Diamond is a precious stone and used in jewellery. It is measured in carats (1 carat = 200 mg).

ALLOTROPE OF OXYGEN FAMILY

Oxygen occurs as two non-metallic forms, dioxygen O_2 and ozone O_3 . Dioxygen O_2 is stable as a diatomic molecule. O_3 molecule is diamagnetic while O_2 is paramagnetic.

Six allotropes of selenium are known.

Tellurium has only one crystalline form, which is silvery white and semimetallic.

This is similar to grey Se, but has stronger metallic interaction.

Sulphur Allotropic forms :

Sulphur forms numerous allotropes of which the yellow rhombic (α -sulphur) and monoclinic (β -sulphur) forms are the most important. The stable form at room temperature is rhombic sulphur, which transforms to monoclinic sulphur when heated above 369 K.

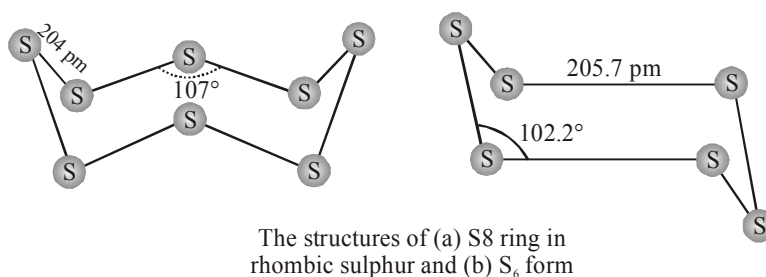
Rhombic sulphur (α -sulphur) (*Most stable sulphur allotrope at room temperature*)

This allotrope is yellow in colour, m.p. 385.8 K and specific gravity 2.06. Rhombic sulphur crystals are formed on evaporating the solution of roll sulphur in CS_2 . It is insoluble in water but dissolves to some extent in benzene, alcohol and ether. It is readily soluble in CS_2 .

Monoclinic sulphur (β -sulphur)

Its m.p. is 393 K and specific gravity 1.98. It is soluble in CS_2 while water insoluble. This form of sulphur is prepared by melting rhombic sulphur in a dish and cooling, till crust is formed. Two holes are made in the crust and the remaining liquid poured out. On removing the crust, colourless needle shaped crystals of β -sulphur are formed. It is stable above 369 K and transforms into α -sulphur below it. Conversely, α -sulphur is stable below 369 K and transforms into β -sulphur above this. At 369 K, both the forms are stable. This temperature is called transition temperature.

Both rhombic and monoclinic sulphur have S_8 molecules. These S_8 molecules are packed to give different crystal structures. The S_8 ring in both the forms is puckered and has a crown shape. The molecular dimensions are given in the figure.



Several other modifications of sulphur containing 6-20 sulphur atoms per ring have been synthesised in the last two decades. In cyclo- S_6 , the ring adopts the chair form and the molecular dimensions are as shown in figure. At elevated temperatures (~ 1000 K), S_2 is the dominant species and is paramagnetic just like O_2 .

Note : Engel's sulphur (ϵ -sulphur) is unstable and contains S_6 rings arranged in the chair conformation. It is made by pouring $Na_2S_2O_3$ solution into concentrated HCl and extracting the S with toluene. Plastic sulphur-(χ) is obtained by pouring liquid sulphur into water.

Example

Which form of sulphur shows paramagnetic behaviour ?

Solution

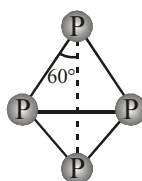
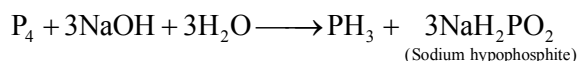
In vapour state sulphur partly exists as S_2 molecule which has two unpaired electrons in the antibonding π^* orbitals like O_2 and, hence, exhibits paramagnetism.

Allotropes of Nitrogen Family :

Solid As, Sb and Bi each exist in several allotropic forms. Arsenic vapour contains tetrahedral As_4 molecules. A reactive yellow form of the solid resembles white phosphorus and is thought to contain tetrahedral As_4 units. Sb also has a yellow form. All three elements have much less reactive metallic or α -forms.

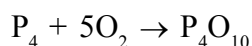
PHOSPHORUS ALLOTROPIC FORMS

Phosphorus is found in many allotropic forms, the important ones being white, red and black. White phosphorus is a translucent, white, waxy solid. It is poisonous, insoluble in water but soluble in carbon disulphide and glows in dark (chemiluminescence). It dissolves in boiling NaOH solution in an inert atmosphere giving PH_3 .



White Phosphorus

White phosphorus is less stable and therefore, more reactive than the other solid phases under normal conditions because of angular strain in the P_4 molecule where the angles are only 60° . It readily catches fire in air to give dense white fumes of P_4O_{10} .

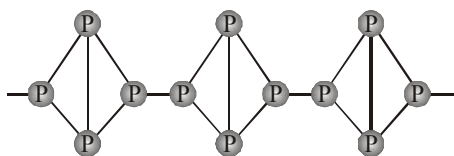


It consists of discrete tetrahedral P_4 molecule as shown in Fig.

Red phosphorus is obtained by heating white phosphorus at 573K in an inert atmosphere for several days. When red phosphorus is heated under high pressure, a series of phases of black phosphorus is formed.

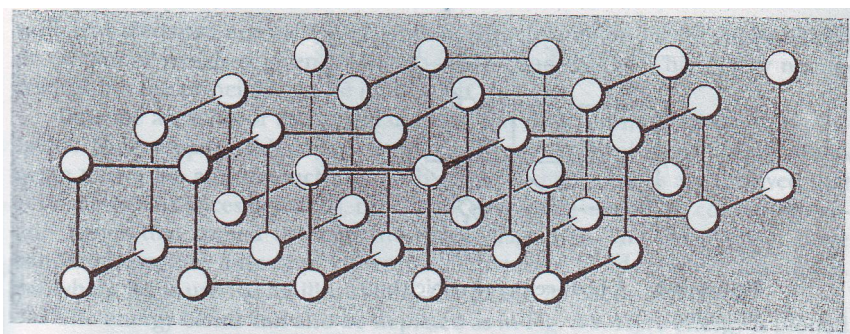
Red phosphorus possesses iron grey lustre. It is odourless, nonpoisonous and insoluble in water as well as in carbon disulphide. Chemically, red phosphorus is much less reactive than white phosphorus. It does not glow in the dark.

It is polymeric, consisting of chains of P_4 tetrahedra linked together in the manner as shown in Fig.



Red Phosphorus

Black phosphorus has two forms α -black phosphorus and β -black phosphorus. α -Black phosphorus is formed when red phosphorus is heated in a sealed tube at 803K. It can be sublimed in air and has opaque monoclinic or rhombohedral crystals. It does not oxidise in air. β -Black phosphorus is prepared by heating white phosphorus at 473 K under high pressure. It does not burn in air upto 673 K.

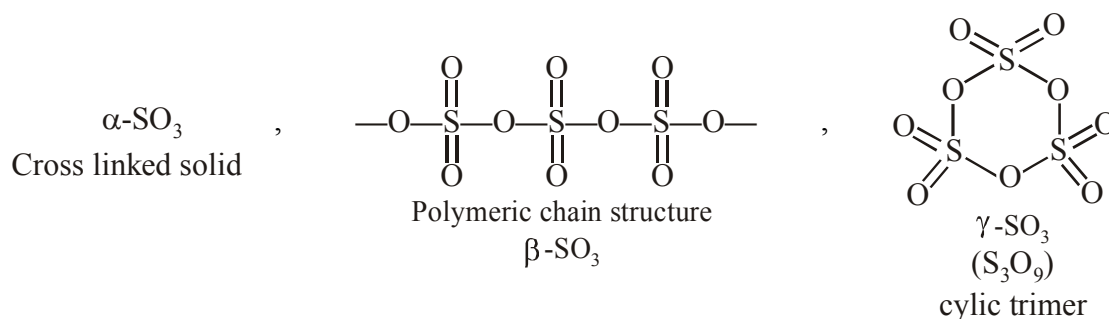


Thermodynamic stability order : Black phosphorus > Red phosphorus > White phosphorus

Reactivity order : Black phosphorus < Red phosphorus < White phosphorus

ALLOTROPIC FORM OF SO_3

SO_3 have three allotropic forms α - SO_3 , β - SO_3 and γ - SO_3



QUESTION OF HYDROGEN BONDING

- Q.1 Explain the structure of Boric acid in solid state.
- Q.2 Boiling point of o-Nitrophenol is less than meta and para nitrophenol. Why?
- Q.3 Maleic acid is more acidic than fumaric acid. Why?
- Q.4 $\text{H}-\text{F}$ is only liquid among halogen acid. Why?
- Q.5 Ammonia is more easily liquefied than HCl , explain.
- Q.6 Why ice floats on water?
- Q.7 Water shows maximum density at 4°C . Why?
- Q.8 HI is the strongest halogen acid, whereas $\text{H}-\text{F}$ is the weakest. Why?
- Q.9 Wood pieces are used to hold ice-cream. Why?
- Q.10 KHF_2 is possible but not KBr_2 or KI_2 . Why?
- Q.11 o-Nitrophenol is less soluble in H_2O than p-Nitrophenol. Why?
- Q.12 o-Hydroxy benzaldehyde is a liquid at room temperature while p-hydroxy benzaldehyde is a high melting solid.
- Q.13 Glycerol is more viscous than ethanol. Explain.
- Q.14 CH_4 and H_2O have nearly same molecular weight. Yet CH_4 has a boiling point 112 K and water 373 K. Explain.
- Q.15 The experimental molecular weight of acetic acid is just double than theoretical molecular weight of acetic acid. Why?
- Q.16 Although chlorine has same electronegativity as nitrogen but the former does not form effective H-bonding. Explain.
- Q.17 Molar entropy change of vapourization of acetic acid is less than that of water. Explain.
- Q.18 Heat of vapourization of water is higher than HF , however strength of H-bond in HF is higher than water. Explain.

EXERCISE # O-1

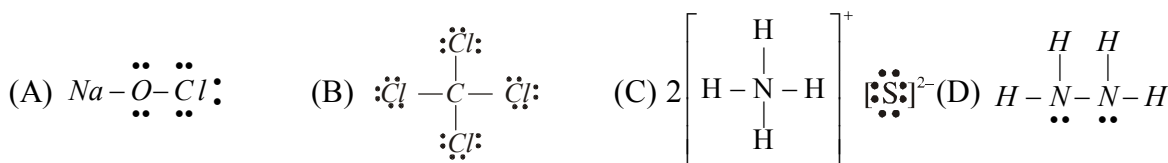
IONIC BOND

(Only one option is correct)

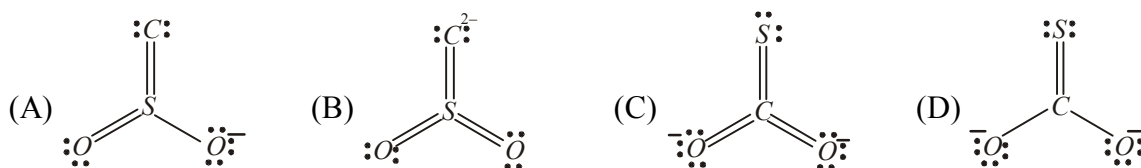
- The compound which contains ionic as well as covalent bonds is
(A) $C_2H_4Cl_2$ (B) CH_3I (C) KCN (D) H_2O_2
- A bond formed between two like atoms cannot be
(A) ionic (B) covalent (C) coordinate (D) metallic
- An ionic bond A^+B^- is most likely to be formed when :
(A) the ionization energy of A is high and the electron gain enthalpy of B is low
(B) the ionization energy of A is low and the electron gain enthalpy of B is high
(C) the ionization energy of A and the electron gain enthalpy of B both are high
(D) the ionization energy of A and the electron gain enthalpy of B both are low

COVALENT BOND, CO-ORDINATE BOND & LEWIS STRUCTURE

- PCl_5 exists but NCl_5 does not because :
(A) Nitrogen has no vacant $2d$ -orbitals (B) NCl_5 is unstable
(C) Nitrogen atom is much smaller than P (D) Nitrogen is highly inert
- Which of the following species are hypervalent?
(1) PCl_5 , (2) BF_3 , (3) XeF_2 , (4) CO_3^{2-}
(A) 1, 2, 3 (B) 1, 3 (C) 3, 4 (D) 1, 2
- The types of bond present in $N_2O_{5(g)}$ are
(A) only covalent (B) only ionic (C) ionic and covalent (D) covalent & coordinate
- Which of the following molecule does not have coordinate bonds?
(A) CH_3-NC (B) CO (C) O_3 (D) CO_3^{2-}
- Which of the following Lewis dot diagrams is(are) incorrect ?



- The possible structure(s) of monothiocarbonate ion is :



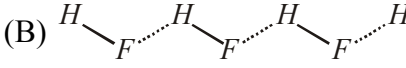
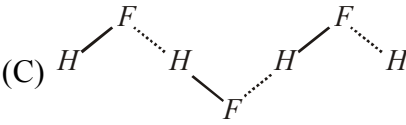
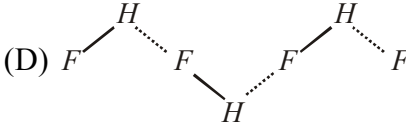
- The valency of sulphur in sulphuric acid is :



V.B.T., HYBRIDISATION & VSEPR THEORY

11. In the following compound $\overset{1}{\text{C}}\text{H}_2 = \overset{2}{\text{C}}\text{H} - \overset{3}{\text{C}}\text{H}_2 - \text{C} \equiv \text{CH}$, the $\text{C}_2 - \text{C}_3$ bond is of the type :
 (A) $\text{sp}-\text{sp}^2$ (B) sp^3-sp^3 (C) $\text{sp}-\text{sp}^3$ (D) sp^2-sp^3
12. Which of the following has a geometry different from the other three species (having the same geometry)?
 (A) BF_4^- (B) SO_4^{2-} (C) XeF_4 (D) PH_4^+
13. Maximum bond energy is in :
 (A) F_2 (B) N_2 (C) O_2 (D) equal
14. The hybridisation and shape of BrF_3 molecule are :
 (A) sp^3d and bent T shape (B) sp^2d^2 and tetragonal
 (C) sp^3d and bent (D) none of these
15. The shape of methyl cation (CH_3^+) is likely to be:
 (A) linear (B) pyramidal (C) planar (D) spherical
16. The structure of XeF_2 involves hybridization of the type :
 (A) sp^3 (B) sp^2 (C) sp^3d (D) sp^3d^2
17. Which of the following has been arranged in increasing order of length of the hybrid orbitals ?
 (A) $\text{sp} < \text{sp}^2 < \text{sp}^3$ (B) $\text{sp}^3 < \text{sp}^2 < \text{sp}$ (C) $\text{sp}^2 < \text{sp}^3 < \text{sp}$ (D) $\text{sp}^2 < \text{sp} < \text{sp}^3$
18. In the context of carbon, which of the following is arranged in the correct order of electronegativity :
 (A) $\text{sp} > \text{sp}^2 > \text{sp}^3$ (B) $\text{sp}^3 > \text{sp}^2 > \text{sp}$ (C) $\text{sp}^2 > \text{sp} > \text{sp}^3$ (D) $\text{sp}^3 < \text{sp} < \text{sp}^2$
19. When $2\text{s}-2\text{s}$, $2\text{p}-2\text{p}$ and $2\text{p}-2\text{s}$ orbitals overlap, the bond strength decreases in the order :
 (A) $\text{p} - \text{p} > \text{s} - \text{s} > \text{p} - \text{s}$ (B) $\text{p} - \text{p} > \text{p} - \text{s} > \text{s} - \text{s}$
 (C) $\text{s} - \text{s} > \text{p} - \text{p} > \text{p} - \text{s}$ (D) $\text{s} - \text{s} > \text{p} - \text{s} > \text{p} - \text{p}$
20. Carbon atoms in $\text{C}_2(\text{CN})_4$ are :
 (A) sp -hybridized (B) sp^2 -hybridized
 (C) sp - and sp^2 hybridized (D) sp , sp^2 and sp^3 - hybridized
21. The bond angle and hybridization in ether (CH_3OCH_3) is :
 (A) $106^\circ 51'$, sp^3 (B) $104^\circ 31'$, sp^3 (C) $> 109^\circ 28'$, sp^3 (D) None of these
22. The structure of XeF_6 in vapour phase is
 (A) pentagonal bipyramidal (B) trigonal bipyramidal
 (C) capped octahedron (D) square bipyramidal

DIPOLE MOMENT & HYDROGEN BONDING

23. Which of the following has been arranged in order of decreasing dipole moment ?
 (A) $\text{CH}_3\text{Cl} > \text{CH}_3\text{F} > \text{CH}_3\text{Br} > \text{CH}_3\text{I}$ (B) $\text{CH}_3\text{F} > \text{CH}_3\text{Cl} > \text{CH}_3\text{Br} > \text{CH}_3\text{I}$
 (C) $\text{CH}_3\text{Cl} > \text{CH}_3\text{Br} > \text{CH}_3\text{I} > \text{CH}_3\text{F}$ (D) $\text{CH}_3\text{F} > \text{CH}_3\text{Cl} > \text{CH}_3\text{I} > \text{CH}_3\text{Br}$
24. The experimental value of the dipole moment of HCl is 1.03 D. The length of the $\text{H}-\text{Cl}$ bond is 1.275 Å. The percentage of ionic character in HCl is nearly :
 (A) 43 (B) 21 (C) 17 (D) 7
25. Ethanol has a higher boiling point than dimethyl ether though they have the same molecular weight. This is due to :
 (A) resonance (B) coordinate bonding
 (C) hydrogen bonding (D) ionic bonding
26. Which of the following compounds would have significant intermolecular hydrogen bonding ?
 HF , CH_3OH , N_2O_4 , CH_4
 (A) HF , N_2O_4 (B) HF , CH_4 , CH_3OH (C) HF , CH_3OH (D) CH_3OH , CH_4
27. For H_2O_2 , H_2S , H_2O and HF , the correct order of decreasing strength of hydrogen bonding is :
 (A) $\text{H}_2\text{O} > \text{HF} > \text{H}_2\text{O}_2 > \text{H}_2\text{S}$ (B) $\text{HF} > \text{H}_2\text{O}_2 > \text{H}_2\text{O} > \text{H}_2\text{S}$
 (C) $\text{HF} > \text{H}_2\text{O} > \text{H}_2\text{O}_2 > \text{H}_2\text{S}$ (D) $\text{H}_2\text{O}_2 > \text{H}_2\text{O} > \text{HF} > \text{H}_2\text{S}$
28. Which one of the following does not have intermolecular H-bonding?
 (A) H_2O (B) *o*-nitro phenol (C) HF (D) CH_3COOH
29. The order of strength of hydrogen bonds is:
 (A) $\text{NH}\cdots\text{N} > \text{OH}\cdots\text{O} > \text{FH}\cdots\text{F}$ (B) $\text{NH}\cdots\text{N} < \text{OH}\cdots\text{O} < \text{FH}\cdots\text{F}$
 (C) $\text{NH}\cdots\text{N} > \text{OH}\cdots\text{O} < \text{FH}\cdots\text{F}$ (D) $\text{NH}\cdots\text{N} < \text{OH}\cdots\text{O} > \text{FH}\cdots\text{F}$
30. The H bond in solid HF can be best represented as:
 (A) $\text{H} - \text{F} \cdots \text{H} - \text{F} \cdots \text{H} - \text{F}$ (B) 
 (C) 
 (D) 

MISCELLANEOUS

31. The formal charges on the three O-atoms in O_3 molecule are
 (A) 0, 0, 0 (B) 0, 0, -1 (C) 0, 0, +1 (D) 0, +1, -1
32. The types of bonds present in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ are
 (A) electrovalent and covalent
 (B) electrovalent, coordinate covalent & H-bond
 (C) covalent, coordinate covalent & H-bonds
 (D) electrovalent, covalent, coordinate covalent & H-bond
33. If ethylene molecule lies in X-Y plane then nodal planes of the π -bond will lie in
 (A) XZ plane (B) YZ plane
 (C) In a plane that bisects C-C axis (D) XY plane
34. Two ice cubes are pressed over each other and unite to form one cube. Which force is responsible for holding them together :
 (A) van der Waal's forces (B) Covalent attraction
 (C) Hydrogen bond formation (D) Dipole-dipole attraction

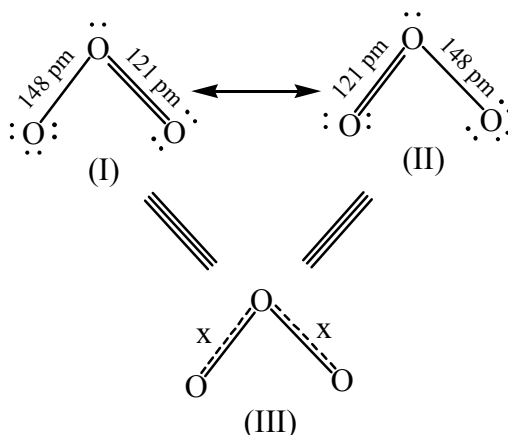
EXERCISE # O-2

IONIC BOND, COVALENT BOND & COORDINATE BOND

- Which of the following compounds contain ionic, covalent and co-ordinate bonds?
(A) NH_4Cl (B) KCN (C) NaBF_4 (D) NaOH
- Which of the following statements is/are true?
(A) Covalent bonds are directional
(B) Ionic bonds are nondirectional
(C) A polar bond is formed between two atoms which have the same electronegativity value.
(D) The presence of polar bonds in a polyatomic molecule suggests that it has zero dipole moment
- To which of the following species octet rule is not applicable :
(A) BrF_5 (B) SF_6 (C) IF_7 (D) CO

LEWIS STRUCTURE & BOND LENGTH

- O_3 (ozone) molecule can be equally represented by the structures I and II shown below



which of the following values of x are not correct

- (A) 148 pm (B) 121 pm (C) less than 121 pm (D) more than 148 pm
- Select the correct statement -
(A) C–O bond length of CO molecule is higher than the C–O bond length of CO_2
(B) C–O bond length of CO molecule is lower than the C–O bond length of CO_2
(C) N–O bond length of NO_3^- ion is higher than the N–O bond length of NO_2^-
(D) N–O bond length of NO_3^- ion is lower than the N–O bond length of NO_2^-

VBT, HYBRIDISATION & VSEPR THEORY

- Which of the following statement(s) is / are not correct?
(A) Hybridization is the mixing of atomic orbitals of large energy difference.
(B) sp^2 -hybrid orbitals are formed from two p - atomic orbitals and one s - atomic orbital
(C) sp^3d^2 -hybrid orbitals are all at 90° to one another
(D) sp^3 -hybrid orbitals are directed towards the corners of a regular tetrahedron
- Which of the following species are linear ?
(A) ICl_2^- (B) I_3^- (C) N_3^- (D) ClO_2^+

8. Which of the following molecules have bent shape.
Where A is central atom, B is surrounding atom and E is lone pair -
(A) AB_2E_2 (B) AB_2E (C) AB_3E (D) AB_2
9. In which of the following process(s) hybridisation of underlined atom does not change -
(A) $\underline{N}H_3 + BF_3 \rightarrow H_3N.BF_3$ (B) $\underline{Si}F_4 + 2F^\ominus \rightarrow [SiF_6]^{2-}$
(C) $BH_3 + \text{cyclopropane} \rightarrow H_3B \leftarrow \text{cyclopropane}$ (D) $H_3\underline{B}O_3 \xrightarrow{OH^-} [B(OH)_4]^-$
10. Which of the following 'd' orbital(s) participate in the hybridisation for Xe in the cationic part of $XeF_6(s)$
(A) d_{xy} (B) $d_{x^2-y^2}$ (C) d_{z^2} (D) d_{y^2}

DIPOLE MOMENT & HYDROGEN BOND

11. Which of the following compounds possesses zero dipole moment?
(A) Water (B) Benzene
(C) Carbon tetrachloride (D) Boron trifluoride
12. Which of the following statements are correct?
(A) The crystal lattice of ice is formed by covalent as well as hydrogen bonds
(B) The density of water increases when heated from 0°C to 4°C
(C) Above 4°C the thermal agitation of water molecules increases. Therefore, intermolecular distance increases and water starts expanding
(D) The density of water decreases from 0°C to a maximum at 4°C
13. In which of the following chemical species hydrogen bonding takes place -
(A) $Na_2HPO_3(s)$ (B) $K_2HPO_4(s)$ (C) $KHCO_3(s)$ (D) $NaHCO_3(s)$

MISCELLANEOUS & STRUCTURE

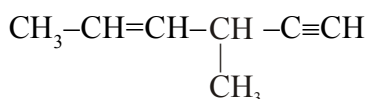
14. Which of the following oxyacids of sulphur contain S-S bonds?
(A) $H_2S_2O_8$ (B) $H_2S_2O_6$ (C) $H_2S_2O_4$ (D) $H_2S_2O_5$
15. Molecule(s) having both polar and non polar bonds is / are
(A) O_2F_2 (B) S_2Cl_2 (C) N_2H_4 (D) S_2F_{10}
16. Which of the following molecule is/are planar -
(A) CH_2Cl_2 (B) $B_3N_3H_6$ (C) SO_3 (D) NF_3

EXERCISE # S-1

Integer Type Answer :

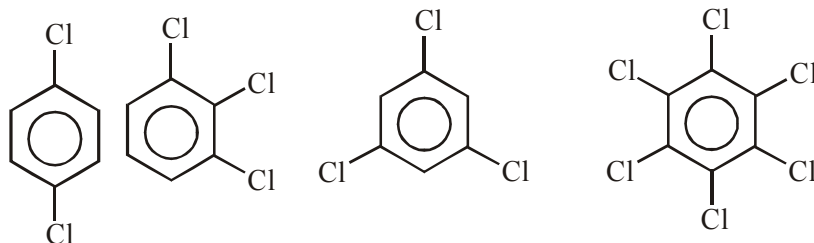
1. In solid NaCl^+ one Na^+ is surrounded by six Cl^- ions find out total number of directional bonds formed by each Na^+ with Cl^- ions.
2. Find out total number of $p\pi-d\pi$ bonds present in SO_2 molecule
3. Find out total number of $p\pi-p\pi$ bonds present in SO_4^{2-}
4. How many number of atomic orbitals are required, so that their mixing produces hybrid orbitals each having % of s-character nearly equal to 17%.
5. Calculate the maximum number of atoms lying in one plane of PCl_3F_2 .
6. Find the lone pair-bond pair ratio for $[\text{SiF}_6]^{2-}$
7. A diatomic molecule has a dipole moment of 1.2 D. If bond length is 1.0 Å, what percentage of an electronic charge exists on each atom.
[Add the digits untill you are getting single digit. e.g. If the answer is 537, then $5 + 3 + 7 = 15$] again $1 + 5 = 6$ and 6 is to be written as answer.

8. Total number of sp^3 hybridised atom(s) in given hydrocarbon.



9. Find the number of lone pair on central atom of ICl_4^-
10. Find the number of acid(s) which are having hypo prefix in it's name from the following.
 H_3PO_4 , H_3BO_3 , H_3PO_3 , H_3PO_2 , HClO_3 , HClO , $(\text{HNO})_2$, $\text{H}_4\text{P}_2\text{O}_6$
11. Find the number of planar molecules/ions which are cyclic –
 $\text{B}_3\text{N}_3\text{H}_6$, $\text{C}_3\text{N}_3\text{Cl}_3$, $(\text{BO}_2^-)_3$, $\text{S}_2\text{O}_8^{2-}$
12. Find the maximum number of plane having maximum number of atoms in CH_4 .

13. Find the number of molecule having dipole moment less than the dipole moment of



14. Find the number of molecules having intramolecular hydrogen bonding in the following :
ice, o-boric acid, o-nitrophenol, o-chlorophenol, chloral hydrate, o-salicylaldehyde
15. Find the number of chemical species which are planar from in the following.
 XeF_5^\ominus , XeF_5^+ , HCN , CO_2 , SO_2

EXERCISE # S-2

(Comprehension) (Q.1 to Q.2)

Bond angle and bond polarity are important parameters associated for bonding in molecule.

- Which of the following bond angle order is incorrect.
 (A) $\text{NH}_3 > \text{PH}_3$ (B) $\text{BF}_3 < \text{BH}_3$
 (C) $\text{O}(\text{CH}_3)_2 < \text{O}(\text{C}_2\text{H}_5)_2$ (D) $\text{CO}_3^{2-} < \text{CO}_2$
- Which of the following molecule is polar and non-planar
 (A) CH_2Cl_2 (B) PCl_5 (C) SO_2 (D) XeF_4

(Comprehension) (Q.3 to Q.4)

During the formation of a covalent bond each participating atom usually acquires electronic configuration to that of nearest noble gas, and the shared electron pair remains localized between the bonded nuclei. Besides these shared electrons there are certain electron pairs which remains localized on C.A. or on substituent or both and are called non bonding or lone pair electrons.

- Which of the following species does / do not follow octet rule:
 (A) Hypovalent (B) Hypervalent
 (C) Odd electron molecules (D) All
- In SO_3^{2-} the total number of lone pairs and bond pairs are respectively
 (A) 18 and 4 (B) 9 and 8 (C) 9 and 4 (D) 7 and 4

(Comprehension) (Q.5 to Q.7)

Hybridisation is a theoretical concept, as state of hybridisation cannot be detected even by spectroscopically; unlike intermediates or transition state in various reactions. but it corrects the predictions which are based simple on overlapping of pure atomic orbitals. VSEPR theory predicts precisely shape and bond angle in a given molecule.

- In which pair of molecules bond angles are not same:
 (A) CCl_4 & SiCl_4 (B) NH_4^+ & NF_4^+ (C) ClF_6^+ & SF_6 (D) None
- The molecules / ions which are planar as well as polar.
 (A) BF_3 , H_2O , HF , NH_2^- (B) SnCl_2 , I_3^+ , NH_2^- , IF_3
 (C) CO_3^{2-} , I_3^- , SF_2 , XeF_2 (D) NO_2^- , XeF_4 , ICl_4^- , NH_2^+
- The correct order of energy levels of hybrid orbitals.
 (A) $sp > sp^2 > sp^3$ (B) $sp < sp^2 < sp^3$ (C) $sp^2 > sp^3 > sp$ (D) $sp^3 > sp > sp^2$

(Comprehension) (Q.8 to Q.10)

As one moves from sp hybridisation to sp^3 . % of s-character in hybrid orbital decreases from 50% to 25% and p-character increases from 50% to 75% and in any hybrid orbital total % of s & p-character remains 100%. By increasing p-character the hybrid orbitals become elongated hence, their overlapping extent decreases that is results into weak bond energy also bond angle decreases.

- Statement-1** : On decreasing s-character in hybrid orbitals, bond angle decreases.
Statement-2 : p-orbitals are at 90° to one another.
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
 (C) Statement-1 is true, statement-2 is false.
 (D) Statement-1 is false, statement-2 is true.

9. The type of overlapping which produces bond of maximum bond energy is:
 (A) $sp^3 - 1s$ (B) $sp^2 - 1s$
 (C) $sp - 1s$ (D) All have same bond energy
10. The molecule having bond pair in which % of s character is minimum for the central atom's hybrid orbital.
 (A) SiF_4 (B) BCl_3 (C) CH_3^+ (D) CO_2

Match the Column :

11. Match the column

Column-I (molecules)

- (A) PCl_5 ($\theta = 120^\circ$, ($\theta' = 90^\circ$)
 (B) NH_3 ($\theta = 107^\circ$)
 (C) SiH_4 ($\theta = 109^\circ 28'$) (R)
 (D) SO_2 ($\theta = 116^\circ$)

Column-II (correct about molecule)

- (P) Number of the given bond angle (θ or θ') is = One
 (Q) Number of the given bond angle (θ or θ') is = Three
 (R) Number of the given bond angle (θ or θ') is = Six
 (S) d-orbital(s) is/are involved in hybridisation of central atom
 (T) Lone pair at underlined atom is present

12. Column I

- (A) BrF_3
 (B) TeF_5^-
 (C) IF_7
 (D) XeF_4

Column II

- (P) Atleast one angle $\leq 90^\circ$
 (Q) Central atom is sp^3d^2 hybridised
 (R) Non planar
 (S) Polar

13. Column I

- (A) $I(CN)_2^-$
 (B) CO_3^{2-}
 (C) XeO_2F_2
 (D) SOF_4

Column II

- (P) Having $p\pi-p\pi$ bond & $\mu_D = 0$
 (Q) Having $p\pi-d\pi$ bond & $\mu_D \neq 0$
 (R) Planar
 (S) Central atom is sp^3d

14. Column I

- (A) $H_2S_2O_5$
 (B) $H_6B_2O_7^{2-}$
 (C) $H_4P_2O_6$ (tetrabasic)
 (D) $H_6Si_2O_7$

Column II

- (P) Central atom is sp^3 hybridised
 (Q) M-O-M i.e. oxo linkage is present
 (R) M-M linkage is present
 (S) Non planar

15. Column-I

- (P) XeF_4
 (Q) BrF_5
 (R) ClF_3
 (S) SO_3^{2-}

Column-II

- (1) sp^3d hybridised with 2 lone pair on central atom
 (2) sp^3d^2 hybridised with 2 lone pair on central atom
 (3) sp^3 hybridised with 1 lone pair on central atom
 (4) sp^3d^2 hybridised with 1 lone pair on central atom

Code :

	P	Q	R	S
(A)	1	2	3	4
(B)	2	4	1	3
(C)	2	4	3	1
(D)	3	1	4	2

16. Column-I

(P) NH_4Cl (Q) $\text{K}[\text{HF}_2]$ (R) $\text{B}_3\text{N}_3\text{H}_6$ (S) SiC

Column-II

(1) diamond like structure

(2) Benzene like structure

(3) Both hydrogen bond and ionic bond exist

(4) Both covalent bond and ionic bond exist

Code :

	P	Q	R	S
(A)	4	3	2	1
(B)	3	4	2	1
(C)	3	4	1	2
(D)	4	1	3	2

MATCHING LIST TYPE 1 × 3 Q. (THREE LIST TYPE Q.)

Column - I	Column - II	Column - III
(P) d_{yz}	(1) p_y	(i) 1 lobe – 1 lobe overlap
(Q) s	(2) p_x	(ii) 2 lobe – 2 lobe overlap
(R) d_{xz}	(3) d_{yz}	(iii) 4 lobe – 4 lobe overlap
(S) p_z	(4) s	(iv) Zero overlap

17. Which of the following combination results in π -bond formation if internuclear axis is z-axis

(A) (P), (1), (ii) (B) (P), (4), (i) (C) (R), (4), (iv) (D) (R), (3), (ii)

18. Which of the following combination results in σ -bond formation if internuclear axis is z-axis

(A) (P), (1), (ii) (B) (Q), (3), (ii) (C) (Q), (4), (i) (D) (R), (2), (ii)


19. Which of the following combination results in δ -bond formation if internuclear axis is x-axis

(A) (P), (1), (i) (B) (P), (3), (iii) (C) (R), (3), (iv) (D) (P), (2), (ii)

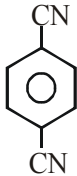
EXERCISE # JEE-MAIN

- Which of the following statements is true ? [AIEEE-2002]
 - HF is less polar than HBr
 - Water does not contain any ions
 - Chemical bond formation takes place when forces of attraction overcome the forces of repulsion
 - In covalent bond, transfer of electrons takes place
- Which one of the following pairs of molecules will have permanent dipole moments for both members [AIEEE-2003]
 - (1) NO_2 and CO_2
 - (2) NO_2 and O_3
 - (3) SiF_4 and CO_2
 - (4) SiF_4 and NO_2
- The pair of species having identical shapes for molecules of both species is [AIEEE-2003]
 - (1) XeF_2 , CO_2
 - (2) BF_3 , PCl_3
 - (3) PF_5 , IF_5
 - (4) CF_4 , SF_4
- The correct order of bond angles (smallest first) in H_2S , NH_3 , BF_3 and SiH_4 is :- [AIEEE-2004]
 - (1) $\text{H}_2\text{S} < \text{NH}_3 < \text{SiH}_4 < \text{BF}_3$
 - (2) $\text{NH}_3 < \text{H}_2\text{S} < \text{SiH}_4 < \text{BF}_3$
 - (3) $\text{H}_2\text{S} < \text{SiH}_4 < \text{NH}_3 < \text{BF}_3$
 - (4) $\text{H}_2\text{S} < \text{NH}_3 < \text{BF}_3 < \text{SiH}_4$
- Lattice energy of an ionic compound depends upon [AIEEE-2005]
 - (1) charge on the ion only
 - (2) size of the ion only
 - (3) packing of the ion only
 - (4) charge and size of the ion
- Of the following sets which one does not contain isoelectronic species ? [AIEEE-2005]
 - (1) PO_4^{3-} , SO_4^{2-} , ClO_4^-
 - (2) CN^- , N_2 , C_2^{2-}
 - (3) SO_3^{2-} , CO_3^{2-} , NO_3^-
 - (4) BO_3^{3-} , CO_3^{2-} , NO_3^-
- In which of the following molecules/ions are all the bonds **not** equal? [AIEEE-2006]
 - (1) XeF_4
 - (2) BF_4^-
 - (3) SF_4
 - (4) SiF_4
- Which of the following hydrogen bonds is the strongest [AIEEE-2007]
 - (1) $\text{F}-\text{H} \cdots \text{F}$
 - (2) $\text{O}-\text{H} \cdots \text{O}$
 - (3) $\text{O}-\text{H} \cdots \text{F}$
 - (4) $\text{O}-\text{H} \cdots \text{N}$
- The hybridisation of orbitals of N atom in NO_3^- , NO_2^+ and NH_4^+ are respectively:- [AIEEE-2011]
 - (1) sp , sp^3 , sp^2
 - (2) sp^2 , sp^3 , sp
 - (3) sp , sp^2 , sp^3
 - (4) sp^2 , sp , sp^3
- The structure of IF_7 is :- [AIEEE-2011]
 - (1) octahedral
 - (2) pentagonal bipyramid
 - (3) square pyramid
 - (4) trigonal bipyramid
- Which of the following has maximum number of lone pairs associated with Xe [AIEEE-2011]
 - (1) XeO_3
 - (2) XeF_4
 - (3) XeF_6
 - (4) XeF_2
- The molecule having smallest bond angle is :- [AIEEE-2012]
 - (1) PCl_3
 - (2) NCl_3
 - (3) AsCl_3
 - (4) SbCl_3
- In which of the following pairs the two species are not isostructural ? [AIEEE-2012]
 - (1) AlF_6^{3-} and SF_6
 - (2) CO_3^{2-} and NO_3^-
 - (3) PCl_4^+ and SiCl_4
 - (4) PF_5 and BrF_5

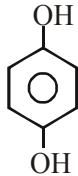
14. The number of S-S bonds in SO_3 , $\text{S}_2\text{O}_3^{2-}$, $\text{S}_2\text{O}_6^{2-}$ and $\text{S}_2\text{O}_8^{2-}$ respectively are :-
[JEE-MAINS-2012]
(1) 1, 0, 1, 0 (2) 0, 1, 1, 0 (3) 1, 0, 0, 1 (4) 0, 1, 0, 1 (On line)
15. Among the following species which two have trigonal bipyramidal shape ? [JEE-MAINS-2012]
(I) NI_3 (II) I_3^- (III) SO_3^{2-} (IV) NO_3^- (On line)
(1) II and III (2) III and IV (3) I and IV (4) I and III
16. Which of the following has the square planar structure :-
[JEE-MAINS-2012]
(1) NH_4^+ (2) CCl_4 (3) XeF_4 (4) BF_4^- (On line)
17. The compound of Xenon with zero dipole moment is :-
[JEE-MAINS-2012]
(1) XeO_3 (2) XeO_2 (3) XeF_4 (4) XeOF_4 (On line)
18. Among the following the molecule with the lowest dipole moment is :- [JEE-MAINS-2012]
(1) CHCl_3 (2) CH_2Cl_2 (3) CCl_4 (4) CH_3Cl (On line)
19. The formation of molecular complex $\text{BF}_3 - \text{NH}_3$ results in a change in hybridisation of boron :-
[JEE-MAINS-2012]
(1) from sp^3 to sp^3d (2) from sp^2 to dsp^2 (On line)
(3) from sp^3 to sp^2 (4) from sp^2 to sp^3
20. Trigonal bipyramidal geometry is shown by:
[JEE-MAINS-2013]
(1) XeO_3F_2 (2) XeOF_2 (3) XeO_3 (4) FXeOSO_2F (On line)
21. Which one of the following molecules is polar?
[JEE-MAINS-2013]
(1) CF_4 (2) SbF_5 (3) IF_5 (4) XeF_4 (On line)
22. Oxidation state of sulphur in anions SO_3^{2-} , $\text{S}_2\text{O}_4^{2-}$ and $\text{S}_2\text{O}_6^{2-}$ increases in the orders :
[JEE-MAINS-2013]
(1) $\text{S}_2\text{O}_6^{2-} < \text{S}_2\text{O}_4^{2-} < \text{SO}_3^{2-}$ (2) $\text{SO}_3^{2-} < \text{S}_2\text{O}_4^{2-} < \text{S}_2\text{O}_6^{2-}$ (On line)
(3) $\text{S}_2\text{O}_4^{2-} < \text{SO}_3^{2-} < \text{S}_2\text{O}_6^{2-}$ (4) $\text{S}_2\text{O}_4^{2-} < \text{S}_2\text{O}_6^{2-} < \text{SO}_3^{2-}$
23. XeO_4 molecule is tetrahedral having :
[JEE-MAINS-2013]
(1) Two $\text{p}\pi\text{-d}\pi$ bonds (2) Four $\text{p}\pi\text{-d}\pi$ bonds (On line)
(3) One $\text{p}\pi\text{-d}\pi$ bond (4) Three $\text{p}\pi\text{-d}\pi$ bonds
24. Bond distance in HF is 9.17×10^{-11} m. Dipole moment of HF is 6.104×10^{-30} Cm. The percent ionic character in HF will be : (electron charge = 1.60×10^{-19} C) [JEE-MAINS-2013]
(1) 61.0% (2) 38.0% (On line)
(3) 35.5% (4) 41.5%
25. The shape of IF_6^- is :
[JEE-MAINS-2013]
(1) distorted octahedron (2) Pyramidal (On line)
(3) Octahedral (4) Square antiprism
26. Which has trigonal bipyramidal shape ?
[JEE-MAINS-2013]
(1) XeOF_4 (2) XeO_3 (3) XeO_3F_2 (4) XeOF_2 (On line)

27. The catenation tendency of C, Si and Ge is in the order $\text{Ge} < \text{Si} < \text{C}$. The bond energies (in kJ mol^{-1}) of C—C, Si—Si and Ge—Ge bonds are respectively : [JEE-MAINS-2013 (On line)]
 (1) 348, 260, 297 (2) 348, 297, 260 (3) 297, 348, 260 (4) 260, 297, 348
28. In which of the following sets, all the given species are isostructural ? [JEE-MAINS-2013 (On line)]
 (1) BF_3 , NF_3 , PF_3 , AlF_3 (2) PCl_3 , AlCl_3 , BCl_3 , SbCl_3
 (3) BF_4^- , CCl_4 , NH_4^+ , PCl_4^+ (4) CO_2 , NO_2 , ClO_2 , SiO_2
29. For which of the following molecule significant $\mu \neq 0$ [JEE-M-2014]
- 

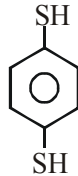
(a)



(b)



(c)



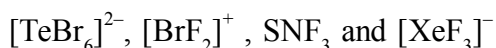
(d)
- (1) Only (c) (2) (c) and (d) (3) Only (a) (4) (a) and (b)
30. Among the following oxoacids, the correct decreasing order of acid strength is :- [JEE-M-2014]
 (1) $\text{HClO}_4 > \text{HClO}_3 > \text{HClO}_2 > \text{HOCl}$ (2) $\text{HClO}_2 > \text{HClO}_4 > \text{HClO}_3 > \text{HOCl}$
 (3) $\text{HOCl} > \text{HClO}_2 > \text{HClO}_3 > \text{HClO}_4$ (4) $\text{HClO}_4 > \text{HOCl} > \text{HClO}_2 > \text{HClO}_3$
31. The number and type of bonds in C_2^{2-} ion in CaC_2 are:
 [AIEEE-2005, AIEEE-2011, JEE-MAINS-2014 (On line)]
 (1) Two σ bonds and one π - bond (2) Two σ bonds and two π - bonds
 (3) One σ bond and two π - bonds (4) One σ bond and one π - bond
32. For the compounds [JEE-MAINS-2014]
 CH_3Cl , CH_3Br , CH_3I and CH_3F , (On line)
 the correct order of increasing C-halogen bond length is :
 (1) $\text{CH}_3\text{F} < \text{CH}_3\text{Br} < \text{CH}_3\text{Cl} < \text{CH}_3\text{I}$ (2) $\text{CH}_3\text{F} < \text{CH}_3\text{Cl} < \text{CH}_3\text{Br} < \text{CH}_3\text{I}$
 (3) $\text{CH}_3\text{Cl} < \text{CH}_3\text{Br} < \text{CH}_3\text{F} < \text{CH}_3\text{I}$ (4) $\text{CH}_3\text{F} < \text{CH}_3\text{I} < \text{CH}_3\text{Br} < \text{CH}_3\text{Cl}$
33. Shapes of certain interhalogen compounds are stated below. Which one of them is not correctly stated? [JEE-MAINS-2014]
 (1) IF_7 : Pentagonal bipyramid (2) BrF_5 : Trigonal bipyramid (On line)
 (3) ICl_3 : Planar dimeric (4) BrF_3 : Planar T-shaped
34. Which of the following molecules has two sigma(σ) and two pi(π) bonds :- [JEE-MAINS-2014]
 (1) HCN (2) $\text{C}_2\text{H}_2\text{Cl}_2$ (3) N_2F_2 (4) C_2H_4 (On line)
35. The species in which the N atom is in a state of sp hybridization is [JEE-MAINS(offline)-2016]
 (1) NO_2 (2) NO_2^+ (3) NO_2^- (4) NO_3^-
36. The pair in which phosphorous atoms have a formal oxidation state of + 3 is :- [JEE-MAINS(offline)-2016]
 (1) Pyrophosphorous and pyrophosphoric acids
 (2) Orthophosphorous and pyrophosphorous acids
 (3) Pyrophosphorous and hypophosphoric acids
 (4) Orthophosphorous and hypophosphoric acids

37. The group of molecules having identical shape is : [JEE-MAINS(online)-2016]
 (1) SF_4 , XeF_4 , CCl_4 (2) ClF_3 , XeOF_2 , XeF_3^+
 (3) PCl_5 , IF_5 , XeO_2F_2 (4) BF_3 , PCl_3 , XeO_3
38. **Assertion :** Among the carbon allotropes, diamond is an insulator, whereas, graphite is a good conductor of electricity. [JEE-MAINS(online)-2016]
Reason : Hybridization of carbon in diamond and graphite are sp^3 and sp^2 , respectively.
 (1) Assertion is incorrect statement, but the reason is correct.
 (2) Both assertion and reason are correct, and the reason is the correct explanation for the assertion.
 (3) Both assertion and reason are incorrect.
 (4) Both assertion and reason are correct, but the reason is not the correct explanation for the assertion.
39. Aqueous solution of which salt will not contain ions with the electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6$? [JEE-MAINS(online)-2016]
 (1) NaCl (2) CaI_2 (3) KBr (4) NaF
40. The correct sequence of decreasing number of π -bonds in the structures of H_2SO_3 , H_2SO_4 and $\text{H}_2\text{S}_2\text{O}_7$ is:- [JEE-MAINS(online)-2017]
 (1) $\text{H}_2\text{S}_2\text{O}_7 > \text{H}_2\text{SO}_4 > \text{H}_2\text{SO}_3$ (2) $\text{H}_2\text{SO}_3 > \text{H}_2\text{SO}_4 > \text{H}_2\text{S}_2\text{O}_7$
 (3) $\text{H}_2\text{S}_2\text{O}_7 > \text{H}_2\text{SO}_3 > \text{H}_2\text{SO}_4$ (4) $\text{H}_2\text{SO}_4 > \text{H}_2\text{S}_2\text{O}_7 > \text{H}_2\text{SO}_3$
41. The increasing order of the boiling points for the following compounds is:- [JEE-MAINS(online)-2017]
 (I) $\text{C}_2\text{H}_5\text{OH}$ (II) $\text{C}_2\text{H}_5\text{Cl}$
 (III) $\text{C}_2\text{H}_5\text{CH}_3$ (IV) $\text{C}_2\text{H}_5\text{OCH}_3$
 (1) (III) < (II) < (I) < (IV) (2) (II) < (III) < (IV) < (I)
 (3) (IV) < (III) < (I) < (II) (4) (III) < (IV) < (II) < (I)
42. The number of P–OH bonds and the oxidation state of phosphorus atom in pyrophosphoric acid ($\text{H}_4\text{P}_2\text{O}_7$) respectively are:- [JEE-MAINS(online)-2017]
 (1) five and four (2) five and five
 (3) four and five (4) four and four
43. The group having triangular planar structures is :- [JEE-MAINS(online)-2017]
 (1) CO_3^{2-} , NO_3^- , SO_3 (2) NCl_3 , BCl_3 , SO_3
 (3) NH_3 , SO_3 , CO_3^{2-} (4) BF_3 , NF_3 , CO_3^{2-}
44. The number of S=O and S–OH bonds present in peroxodisulphuric acid and pyrosulphuric acid respectively are : [JEE-MAINS(online)-2017]
 (1) (2 and 4) and (2 and 4) (2) (4 and 2) and (2 and 4)
 (3) (2 and 2) and (2 and 2) (4) (4 and 2) and (4 and 2)

EXERCISE # JEE-ADVANCED

Integer Type :

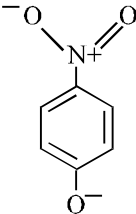
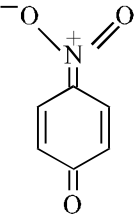
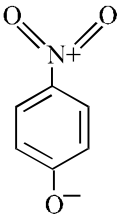
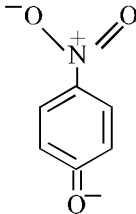
- The number of water molecule(s) directly bonded to the metal centre in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is [JEE 2009]
- Based on VSEPR theory, the number of 90 degree F–Br–F angles in BrF_5 is [JEE 2010]
- The difference in the oxidation numbers of the two types of sulphur atoms in $\text{Na}_2\text{S}_4\text{O}_6$ is. [JEE 2011]
- The total number of lone-pairs of electrons in melamine is [JEE Adv. 2013]
- The sum of the number of lone pairs of electrons on each central atom in the following species is. [JEE 2017]



[Atomic number : N = 7, F = 9, S = 16, Br = 35, Te = 52, Xe = 54]

One or more than one correct :

- The linear structure is assumed by : [IIT-1991]
(A) SnCl_4 (B) NCO^- (C) CS_2 (D) NO_2^+
- Which of the following has zero dipole moment ? [IIT-1993]
(A) ClF (B) PCl_3 (C) SiF_4 (D) CFC_3
- Among the following molecules, which one is planar ? [IIT-1994]
(A) BCl_3 (B) SO_2Cl_2 (C) NH_3 (D) NF_3
- Which of the following species is / are non-linear ? [IIT-1995]
(A) H_2S (B) NH_3 (C) CO_2 (D) SO_2
- Which contains both polar and non-polar bonds ? [IIT-1997]
(A) CH_4 (B) HCN (C) H_2O_2 (D) NH_4Cl
- Which of the following compounds has sp^2 hybridisation ? [IIT-1997]
(A) CO_2 (B) SO_2 (C) N_2O (D) CO
- Which one of the following molecules is planar ? [IIT-1996]
(A) NF_3 (B) NCl_3 (C) BF_3 (D) PH_3
- The number and type of bonds between two carbon atoms in CaC_2 are : [IIT-1996]
(A) 1σ and 1π (B) 1σ and 2π (C) 1σ and 1.5π (D) 1σ
- Among the species NF_3 , NO_3^- , BF_3 , H_3O^+ and HN_3 , identify the isostructural species : [IIT-1996]
(A) (NF_3 , NO_3^-) and (BF_3 , H_3O^+) (B) (NF_3 , HN_3) and (NO_3^- , BF_3)
(C) (NF_3 , H_3O^+) and (NO_3^- , BF_3) (D) (NF_3 , H_3O^+) and (HN_3 , BF_3)
- Among the following the one that is polar and has the central atom with sp^2 hybridisation is : [IIT-1997]
(A) H_2CO_3 (B) SiF_4 (C) BF_3 (D) HClO_2
- The geometry & the type of hybrid orbitals present about the central atom in BF_3 is : [JEE '98]
(A) linear, sp (B) trigonal planar, sp^2
(C) tetrahedral sp^3 (D) pyramidal, sp^3

17. Which one of the following statement (s) is (are) correct? [JEE 1998]
 (A) The electronic configuration of Cr is $[\text{Ar}] 3d^5 4s^1$. (Atomic No. of Cr = 24)
 (B) The magnetic quantum number may have a negative value
 (C) In silver atom, 23 electrons have a spin of one type and 24 of the opposite type. (Atomic No. of Ag = 47)
 (D) The oxidation state of nitrogen in HN_3 is -3.
18. Element X is strongly electronegative and element Y is strongly electropositive. Both are univalent. The compound formed would be : [JEE 1998]
 (A) $\text{X}^+ \text{Y}^-$ (B) $\text{X}^- \text{Y}^+$ (C) $\text{X}^+ \text{Y}^-$ (D) $\text{Y}^+ \text{X}^-$
19. The correct order of increasing C - O bond length of, CO , CO_3^{2-} , CO_2 is [JEE '99]
 (A) $\text{CO}_3^{2-} < \text{CO}_2 < \text{CO}$ (B) $\text{CO}_2 < \text{CO}_3^{2-} < \text{CO}$
 (C) $\text{CO} < \text{CO}_3^{2-} < \text{CO}_2$ (D) $\text{CO} < \text{CO}_2 < \text{CO}_3^{2-}$
20. The geometry of H_2S and its dipole moment are [JEE '99]
 (A) angular & non zero (B) angular & zero
 (C) linear & non zero (D) linear & zero
21. In compounds type ECl_3 , where E = B, P, As or Bi, the angles Cl - E - Cl for different E are in the order [JEE '99]
 (A) $\text{B} > \text{P} = \text{As} = \text{Bi}$ (B) $\text{B} > \text{P} > \text{As} > \text{Bi}$
 (C) $\text{B} < \text{P} = \text{As} = \text{Bi}$ (D) $\text{B} < \text{P} < \text{As} < \text{Bi}$
22. The most likely representation of resonance structure of p-nitrophenoxide is:
 (A)  (B)  (C)  (D) 
23. Amongst H_2O , H_2S , H_2Se and H_2Te , the one with the highest boiling point is [JEE 2000]
 (A) H_2O because of hydrogen bonding
 (B) H_2Te because of higher molecular weight
 (C) H_2S because of hydrogen bonding
 (D) H_2Se because of lower molecular weight
24. The hybridization of atomic orbitals of nitrogen in NO_2^+ , NO_3^- and NH_4^+ are [JEE 2000]
 (A) sp^2 , sp^3 and sp^2 respectively (B) sp , sp^2 and sp^3 respectively
 (C) sp^2 , sp and sp^3 respectively (D) sp^2 , sp^3 and sp respectively
25. The correct order of hybridization of the central atom in the following species NH_3 , PtCl_4^{2-} , PCl_5 and BCl_3 is [JEE 2001]
 (A) dsp^2 , sp^3d , sp^2 and sp^3 (B) sp^3 , dsp^2 , sp^3d , sp^2
 (C) dsp^2 , sp^2 , sp^3 , sp^3d (D) dsp^2 , sp^3 , sp^2 , sp^3d

26. Specify hybridization of N and B atoms in a 1 : 1 complex of BF_3 and NH_3 [JEE 2002]
 (A) N : tetrahedral, sp^3 ; B : tetrahedral, sp^3
 (B) N : pyramidal, sp^3 ; B : pyramidal, sp^3
 (C) N : pyramidal, sp^3 ; B : planar, sp^2
 (D) N : pyramidal, sp^3 ; B : tetrahedral, sp^3
27. The nodal plane in the π -bond of ethene is located in [JEE 2002]
 (A) the molecular plane
 (B) a plane parallel to the molecular plane
 (C) a plane perpendicular to the molecular plane which bisects, the carbon-carbon σ bond at right angle
 (D) a plane perpendicular to the molecular plane which contains, the carbon-carbon bond.
28. Which of the following are isoelectronic and isostructural ? NO_3^- , CO_3^{2-} , ClO_3^- , SO_3 [JEE 2003]
 (A) NO_3^- , CO_3^{2-} (B) SO_3 , NO_3^- (C) ClO_3^- , CO_3^{2-} (D) CO_3^{2-} , SO_3
29. Which species has the maximum number of lone pair of electrons on the central atom ? [JEE 2005]
 (A) ClO_3^- (B) XeF_4 (C) SF_4 (D) I_3^-
30. The percentage of p-character in the orbitals forming P–P bonds in P_4 is [JEE 2007]
 (A) 25 (B) 33 (C) 50 (D) 75
31. The structure of XeO_3 is [JEE 2007]
 (A) linear (B) planar (C) pyramidal (D) T-shaped
32. **Statement-1** : p-Hydroxybenzoic acid has a lower boiling point than o-hydroxybenzoic acid.
because
Statement-2 : o-Hydroxybenzoic acid has intramolecular hydrogen bonding. [JEE 2007]
 (A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
 (B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
 (C) Statement-1 is True, Statement-2 is False.
 (D) Statement-1 is False, Statement-2 is True.
33. **Statement-1** : In water, orthoboric acid behaves as a weak monobasic acid.
because
Statement-2 : In water, orthoboric acid acts as a proton donor. [JEE 2007]
 (A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
 (B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
 (C) Statement-1 is True, Statement-2 is False.
 (D) Statement-1 is False, Statement-2 is True.

34. The nitrogen oxide(s) that contain(s) N–N bond(s) is/are [JEE 2009]
(A) N_2O (B) N_2O_3 (C) N_2O_4 (D) N_2O_5
35. The species having pyramidal shape is/are : [JEE 2010]
(A) SO_3 (B) BrF_3 (C) SiO_3^- (D) OSF_2
36. Which ordering of compounds is according to the decreasing order of the oxidation state of nitrogen- [JEE 2012]
(A) HNO_3 , NO , NH_4Cl , N_2 (B) HNO_3 , NO , N_2 , NH_4Cl
(C) HNO_3 , NH_4Cl , NO , N_2 (D) NO , HNO_3 , NH_4Cl , N_2
37. The shape of XeO_2F_2 molecule is : [JEE 2012]
(A) Trigonal bipyramidal (B) Square planar
(C) tetrahedral (D) see-saw
38. The compound(s) with TWO lone pairs of electrons on the central atom is(are) [JEE 2016]
(A) BrF_5 (B) ClF_3 (C) XeF_4 (D) SF_4
39. The crystalline form of borax has [JEE 2016]
(A) Tetranuclear $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$ unit
(B) All boron atoms in the same plane
(C) Equal number of sp^2 and sp^3 hybridized boron atoms
(D) One terminal hydroxide per boron atom
40. The order of the oxidation state of the phosphorus atom in H_3PO_2 , H_3PO_4 , H_3PO_3 and $\text{H}_4\text{P}_2\text{O}_6$ is [JEE 2017]
(A) $\text{H}_3\text{PO}_4 > \text{H}_4\text{P}_2\text{O}_6 > \text{H}_3\text{PO}_3 > \text{H}_3\text{PO}_2$
(B) $\text{H}_3\text{PO}_3 > \text{H}_3\text{PO}_2 > \text{H}_3\text{PO}_4 > \text{H}_4\text{P}_2\text{O}_6$
(C) $\text{H}_3\text{PO}_2 > \text{H}_3\text{PO}_3 > \text{H}_4\text{P}_2\text{O}_6 > \text{H}_3\text{PO}_4$
(D) $\text{H}_3\text{PO}_4 > \text{H}_3\text{PO}_2 > \text{H}_3\text{PO}_3 > \text{H}_4\text{P}_2\text{O}_6$

ANSWERS KEY

EXERCISE # O-1

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	C	A	B	A	B	D	D	A	D	D
Que.	11	12	13	14	15	16	17	18	19	20
Ans.	D	C	B	A	C	C	A	A	B	C
Que.	21	22	23	24	25	26	27	28	29	30
Ans.	C	C	A	C	C	C	C	B	B	C
Que.	31	32	33	34						
Ans.	D	D	D	C						

EXERCISE # O-2

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	A, C	A, B	A, B, C	A, B, C, D	B, C	A, C	A, B, C	A, B	A, C	B, C
Que.	11	12	13	14	15	16				
Ans.	B, C, D	A, B, C	B, C, D	B, C, D	A, B, C, D	B, C				

EXERCISE # S-1

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	0	1	0	6	4	3	7 (25%)	3	2	4
Que.	11	12	13	14	15					
Ans.	3	10	3	4	4					

EXERCISE # S-2

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	B	A	D	C	D	B	B	B	C	A
Que.	11				12					
Ans.	(A)→Q,R,S;(B)→Q,T;(C)→R;(D)→P,T				(A)→P,S (B)→P,Q,R,S (C)→P,R (D)→P,Q					
Que.	13					14				
Ans.	(A)→P,R,S (B)→P,R (C)→Q,S (D)→Q,S					(A)→P,R,S (B)→P,Q,S (C)→P,R,S (D)→P,Q,S				
Que.	15	16	17	18	19					
Ans.	B	A	A	C	B					

EXERCISE # JEE-MAIN

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	3	2	1	1	4	3	3	1	4	2
Que.	11	12	13	14	15	16	17	18	19	20
Ans.	4	4	4	2	BONUS	3	3	3	4	1
Que.	21	22	23	24	25	26	27	28	29	30
Ans.	3	3	2	4	1	3	2	3	2	1
Que.	31	32	33	34	35	36	37	38	39	40
Ans.	3	2	2	1	2	2	2	4	4	1
Que.	41	42	43	44						
Ans.	4	3	1	4						

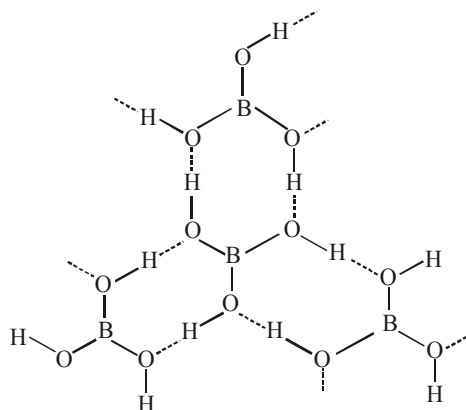
EXERCISE # JEE-ADVANCED

- Ans. 4
- Ans. 0
- Ans. 5
- Ans. 6
- Ans. 6

Que.	6	7	8	9	10	11	12	13	14	15
Ans.	B, C, D	C	A	A, B, D	C	B	C	B	C	A
Que.	16	17	18	19	20	21	22	23	24	25
Ans.	B	A,B,C	B	D	A	B	A	A	B	B
Que.	26	27	28	29	30	31	32	33	34	35
Ans.	A	A	A	D	D	C	D	C	A,B,C or A,C	D
Que.	36	37	38	39	40					
Ans.	B	D	B,C	A,C,D	A					

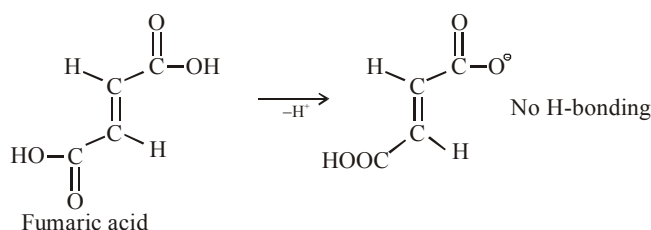
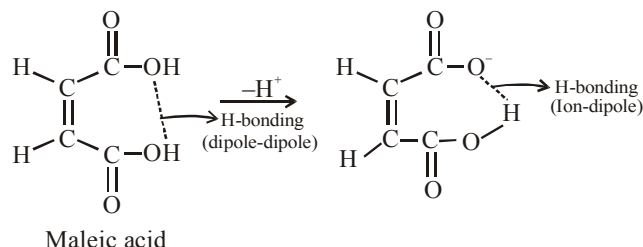
ANSWER OF HYDROGEN BONDING

1.

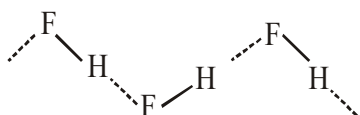


Structure of boric acid; the dotted lines represent hydrogen bonds

- Inter molecular H-Bonding in case of para nitro phenol is strong enough to increase boiling point which is not favoured in o-Nitro phenol.
- Maleic acid anion gets stabilize due to intra molecular H-bonding which is not possible in anion of Fumaric acid. So H^+ releasing tendency is more in case of maleic acid

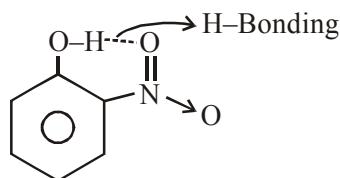


- Due to strong H-Bonding in $H-F$



- Due to H-Bonding in NH_3 .
- Density of ice is higher than that of water due to cage like structure of ice volume of ice increases and density decreases.
- On heating ice in temperature range $0-4^\circ C$ H-bonds of ice break down, which decreases volume, hence density of H_2O increases. On heating ice after $4^\circ C$ thermal vibrations of H_2O molecules increases which increases effective volume of ice, so density of ice again decreases.
- H-I bond is weak as compare to H-F so it can be dissociated easily and can give H^+ easily.
- The organic matter in wood participate in H-bonding with water molecules in ice-cream.
- $K^+[F-H \cdots F]^-$ But $KHBr_2$ & KHI_2 can't form H-Bond.

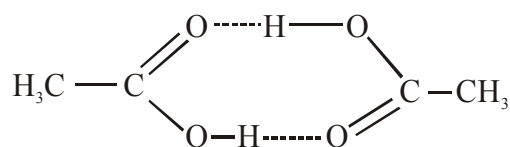
H-bonding
- In o-Nitrophenol intra molecular H-bond is present which decreases it's solubility in water.



Ortho Nitro-phenol

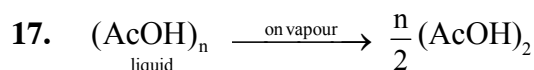
- In o-hydroxy benzaldehyde intramolecular H-bond is present which is less stronger than intermolecular H-bond in p-hydroxy benzaldehyde.
- Extent of H-bonding in glycerol is more as compare to ethanol so it is more viscous.
- Due to H-bonding in H_2O

15. Due to H-bonding in acetic acid it forms dimer so overall molecular weight is just double of original

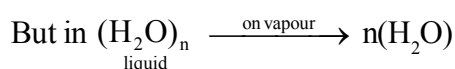


Dimer of CH_3COOH

16. Due to bigger size of 'Cl' atom it's interaction is not enough to evolve the amount of energy which lies in the range of H-bond.



} Not completely converted



Here all H_2O molecule gets vapourised. So entropy change is more

18. As extent of H-bond is more in H_2O as compare to HF, heat of vaporisation of water is higher than HF.

**CHEMICAL BONDING,
COORDINATION CHEMISTRY
& METALLURGY**

ALLU
Session 2019-20

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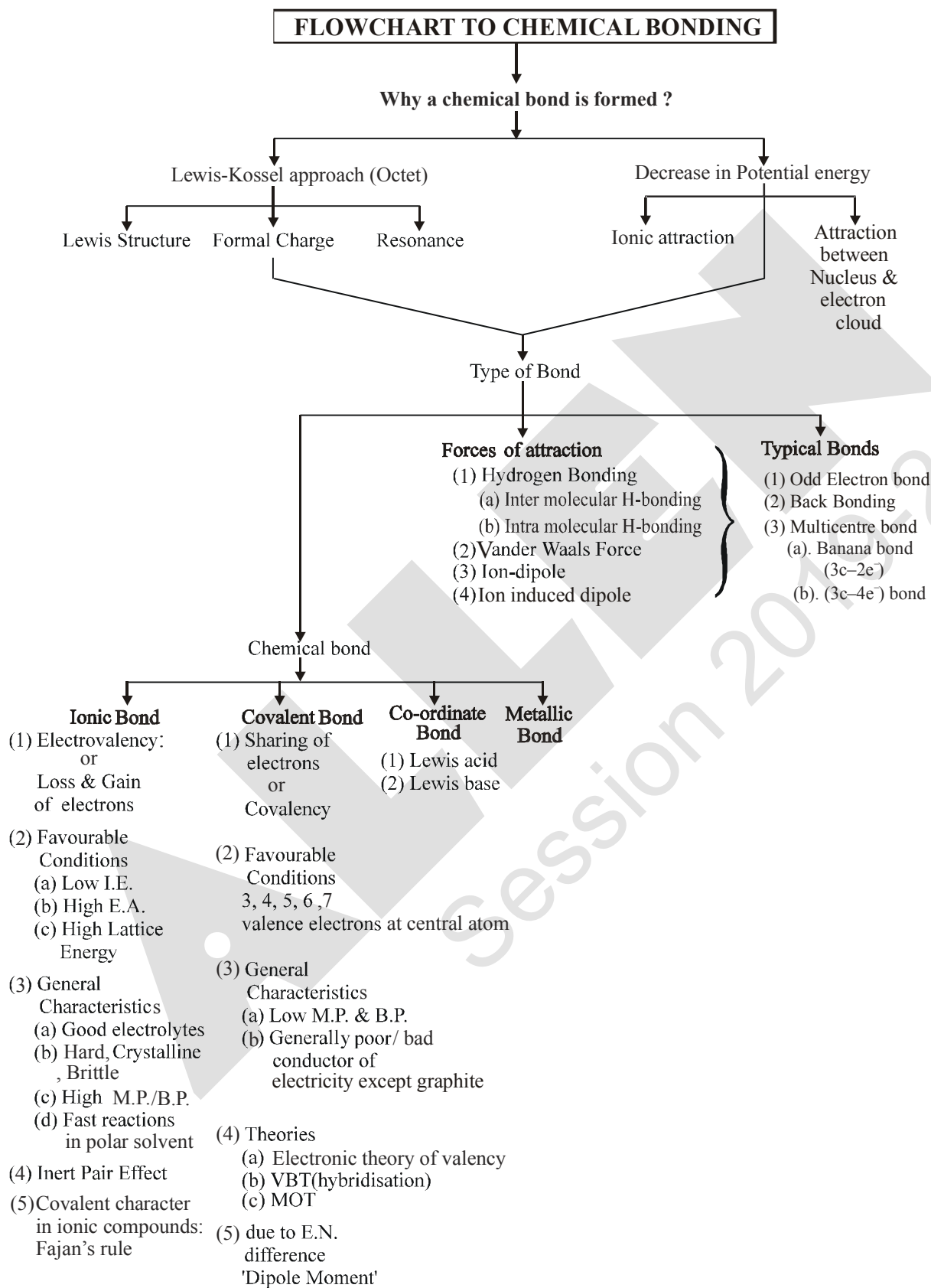
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CHEMICAL BONDING



Note : Hydrogen bond is an extreme manifestation of dipole dipole interaction.

VANDER WAAL'S FORCES

- ⇒ These are the weakest type of inter molecular forces that exist among the chemical species which bring significant change in physical properties.
- ⇒ These are non-directional, non-valence cohesive forces. These attractive forces being played between the two molecules are independent of the presence of other molecules.
- ⇒ Solid, liquid or gaseous states of many molecules are explained on the basis of inter molecular forces other than covalent, ionic or metallic bonds. Although inert gases do not form any type of bond but may exist in liquid and solid states. This shows that the atoms of inert gases are attracted by each other through some type of inter molecular forces. These intermolecular forces are called Vander Waals forces.

Types of Vander Waal's Forces

- (1) **Dipole-dipole interaction (Keesom forces) :** The force of attraction between the oppositely charged poles of two polar molecules (for example : H_2S , HCl , PH_3 etc.) is called dipole-dipole attraction.
- (2) **Dipole-induced dipole interaction (Debye forces) :** This type of cohesive forces occurs in a mixture of polar and non polar molecules. The former induce polarity in non polar molecules by disturbing their electron system. for example force of attraction between Cl_2 and H_2O .
- (3) **Instantaneous dipole-Induced dipole interaction (Dispersion forces/London forces) :** The weak intermolecular forces operating in similar non polar gaseous molecules are called London forces. These forces are very weak in nature and exists only at low temperature. For example weak intermolecular forces in F_2 , Cl_2 , N_2 , molecules and in noble gases.

(Note :- London forces present in both polar and non polar species)

Other Weak Interactions

- (1) **Ion-dipole interaction :** Polar molecules are attracted by ions. The negative pole is attracted by cation and positive pole attracted by the anion. This type of attraction is called ion dipole attraction, ion-dipole attraction is observed generally in the process of solvation when sodium chloride ($\text{Na}^+ \text{Cl}^-$) is dissolved in water because negative poles of water aggregate around Na^+ ions and positive poles around Cl^- ions.
- (2) **Ion-induced dipole interaction :** When non polar molecules come in contact with ions, its electron cloud gets polarised and the oppositely charged end of it is attracted by the ion. For example attraction between I^- and I_2 molecule.

HYBRIDISATION

The phenomenon of intermixing of the orbitals of slightly different energies so as to redistribute their energies, resulting in the formation of new set of orbitals of equivalent energies and shape. For example when one 2s and three 2p-orbitals of carbon hybridise, there is the formation of four new sp^3 hybrid orbitals.

Salient features of hybridisation: The main features of hybridisation are as under :

1. The number of hybrid orbitals is equal to the number of the atomic orbitals that get hybridised.
2. The hybridised orbitals are equivalent in energy and shape.
3. The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.
4. These hybrid orbitals are directed in space in some preferred direction to have minimum repulsion between electron pairs and thus a stable arrangement. Therefore, the type of hybridisation indicates the geometry of the molecules.

Important conditions for hybridisation

- (i) The orbitals present in the valence shell of the atom are hybridised.
- (ii) The orbitals undergoing hybridisation should have almost equal energy.
- (iii) Promotion of electron is not essential condition prior to hybridisation.
- (iv) It is not necessary that only half filled orbitals participate in hybridisation. In some cases, even filled orbitals of valence shell take part in hybridisation.

Types of Hybridisation

There are various types of hybridisation involving s, p and d orbitals. The different types of hybridisation are as under :

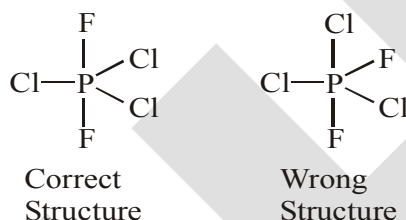
- (i) sp hybridisation (ii) sp^2 hybridisation (iii) sp^3 hybridisation
- (iv) sp^3d hybridisation: (v) sp^3d^2 hybridisation: (vi) sp^3d^3 hybridisation:

BENT'S RULE

- (i) A lone pair of electron prefers to occupy that hybrid orbital which has greater percentage of s-character.
- (ii) A more electronegative atom/group prefers to occupy that hybrid orbital which has smaller percentage of s-character.

Ex. Draw the geometry of PCl_3F_2

Sol.



Because highly electronegative atom occupy axial position (axial position has smaller percentage of s-character).

DRAGO'S RULE

On the basis of experimental bond angles of certain molecules fulfilling the following three conditions,

- (i) Central atom belongs to third or lower period in periodic table
- (ii) Central atom must contain atleast one lone pair of electron
- (iii) Electronegativity of surrounding atom is ≤ 2.5

Drago generalised that in such molecules justification of experimental bond angle can be made satisfactory if one considers no hybridisation, i.e., overlapping of almost pure atomic orbitals from central atom.

In such molecules bond angle is approximately 90° .

Group 15	Bond angle	Group 16	Bond angle
NH_3	$107^\circ 48'$	H_2O	$104^\circ 28'$
PH_3	$93^\circ 36'$	H_2S	92°
AsH_3	$91^\circ 48'$	H_2Se	91°
SbH_3	$91^\circ 18'$	H_2Te	90.5°

- Right order of bond angle.

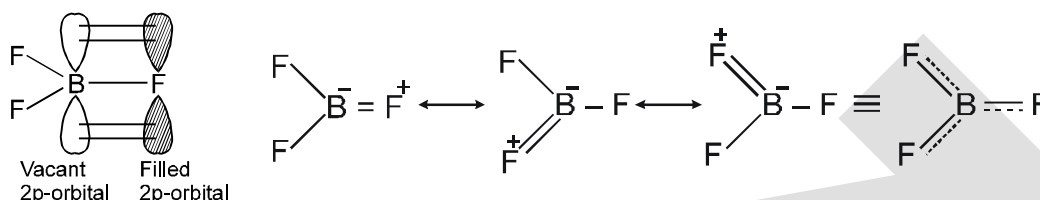
(a) $H_2O > H_2S > H_2Se > H_2Te$

(b) $NH_3 > PH_3 > AsH_3 > SbH_3$

ELECTRON DEFICIENT BONDING**(a) Back Bonding**

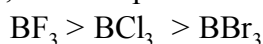
Back bonding generally takes place when out of two bonded atoms one of the atom has vacant orbitals (generally this atom is from second or third period) and the other bonded atom is having some non-bonded electron pair (generally this atom is from the second period). Back bonding increases the bond strength and decreases the bond length.

For example, in BF_3 the boron atom completes its octet by accepting 2p-electrons of fluorine into 2p empty orbital.



- Decrease in B – F bond length is due to delocalised π – π back bonding between filled p-orbital of F atom and vacant p-orbital of B atom.

The extent of back bonding is much larger if the orbitals involved in the back bonding are of same size, for example the extent of back bonding in boron trihalides is as follows :

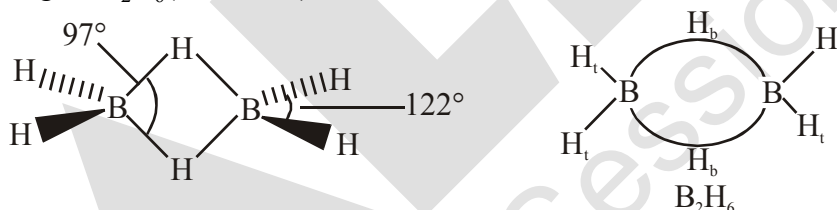


There is π – π back bonding in boron trihalide. The extent of back bonding decreases from BF_3 to BI_3 because of increasing size of p-orbitals participating in back bonding that is from 2p (in F) to 5p (in I).

(b) Bridge Bonding

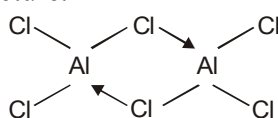
There are many compounds in which some electron deficient bonds are present apart from normal covalent bonds or coordinate bonds which are 2c–2e[–] bonds (two centre two electron bonds). These electron deficient bonds have less number of electrons than the expected such as three centre-two electron bonds (3c–2e) which are present in diborane B_2H_6 , $\text{Al}_2(\text{CH}_3)_6$, $\text{BeH}_2(\text{s})$ etc.

bonding in B_2H_6 (diborane)



The structure of diborane containing four terminal(t) and two bridging(b) hydrogen atoms. The model determined by molecular orbital theory indicates that the bonds between boron and the terminal hydrogen atoms are conventional 2c–2e[–] covalent bonds. The bonding between the boron atoms and the bridging hydrogen atoms is, however different from that in molecules such as hydrocarbons. Having used two electrons in bonding to the terminal hydrogen atoms, each boron has one valence electron remaining for additional bonding. The bridging hydrogen atoms provide one electron each. Thus the B_2H_2 ring is held together by four electrons, an example of 3c–2e bonding. This type of bond is sometimes called as '**banana bond**'. Group 13, gallium is known to form a similar compound, digallane, Ga_2H_6 .

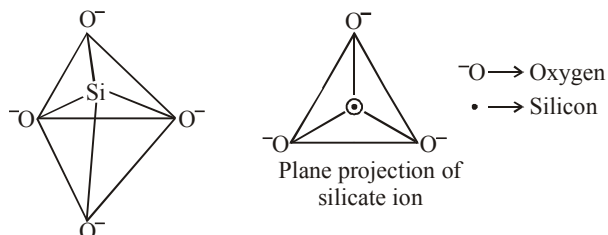
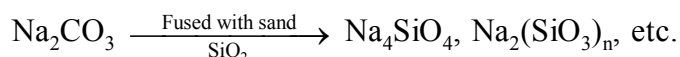
But Al_2Cl_6 have covalent bond only and there is no electron deficient bonding as depicted in the given structure.



(Al – Cl – Al is 3c – 4e bond)

SILICATES

Silicates are metal derivatives of silicic acid, H_4SiO_4 or $\text{Si}(\text{OH})_4$. Silicates are formed by heating metal oxide or metal carbonates with sand, e.g.,



Silicates have basic unit of SiO_4^{4-} , each silicon atom is bonded with four oxide ions tetrahedrally. There are following types of silicates

Silicates	Sharing of O-atom / Basic Tetrahedral unit	Contribution of O-atom/Basic Tetrahedral unit	General formula
Ortho	0	4	SiO_4^{4-}
Pyro	1	3.5	$\text{Si}_2\text{O}_7^{6-}$
Cyclic	2	3	$(\text{SiO}_3)_n^{2n-}$ (n = finite)
Simple chain (pyroxene)	2	3	$(\text{SiO}_3)_n^{2n-}$ (n = infinite)
Double chain (Amphibole)	(3, 2) avg. = 2.5	$\frac{11}{4} = \left(\frac{5.5}{2}\right)$	$(\text{Si}_4\text{O}_{11})_n^{6n-}$
2D or (Sheet)	3	2.5	$(\text{Si}_2\text{O}_5)_n^{2n-}$
3D	4	2	$(\text{SiO}_2)_n$

INERT PAIR EFFECT

In p-block elements the stability of the lower oxidation state increases on descending the group. Because increased effective nuclear charge holds ns electrons tightly due to poor shielding effect of inner d & f orbitals and thereby, restrict their (ns electrons) participation in bonding only np electrons take part in bond formation. As a result of this, +1 oxidation state of Tl is more stable than its +3 oxidation state. Pb shows +2 stable oxidation state and Bi shows +3 stable oxidation state.

For example :

Group 13

B (+3)
 Al (+3)
 Ga (+3), (+1)
 In (+3), (+1)
 Tl (+3), (+1)

Group 14

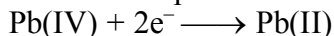
C (+4)
 Si (+4)
 Ge (+4), (+2)
 Sn (+4), (+2)
 Pb (+4), (+2)

Order of stability : $\text{Tl}^{+1} > \text{In}^{+1} > \text{Ga}^{+1}$ (due to inert pair effect)

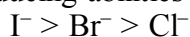
Order of stability : $\text{Pb}^{+2} > \text{Sn}^{+2} > \text{Ge}^{+2}$ (due to inert pair effect)

Ex. PbCl_4 is stable at room temperature whereas PbI_4 doesn't exist.

Sol. Due to inert pair effect $\text{Pb}(+4)$ is less stable than $\text{Pb}(+2)$. Hence it is very good oxidant.



Reducing abilities of halides follows the sequence



MOLECULES THAT DO NOT EXIST

(1) SF_4 , SF_6 & PF_5 exist while OF_4 , OF_6 , NF_5 do not exist

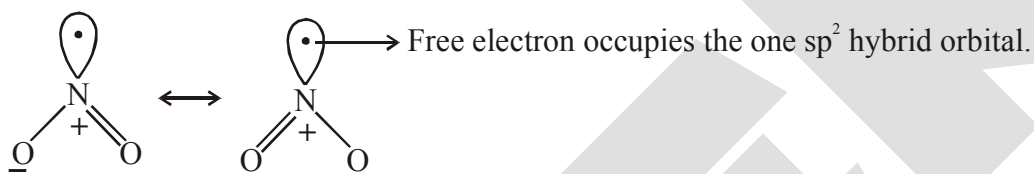
(2) (a) $\text{PI}_5(\text{vap})$ does not exist

(b) PI_5 (Solid) exist

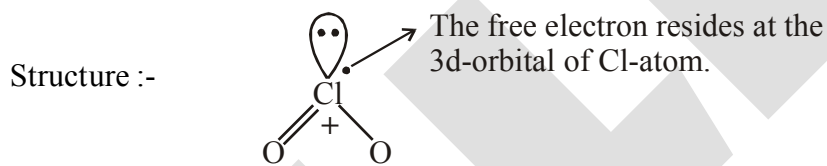
(3) SF_6 , PF_5 , XeF_6 , XeF_4 & XeF_2 exist while SH_6 , PH_5 , XeH_6 , XeH_4 , XeH_2 do not exist

STRUCTURE OF ODD ELECTRONIC SPECIES

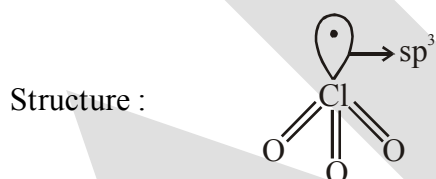
(1) NO_2



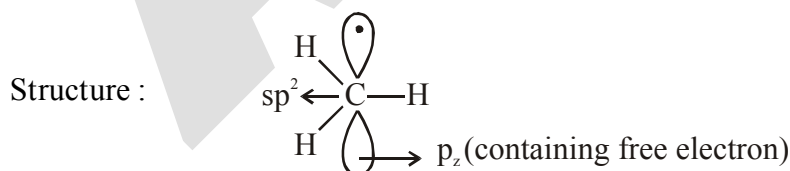
(2) ClO_2



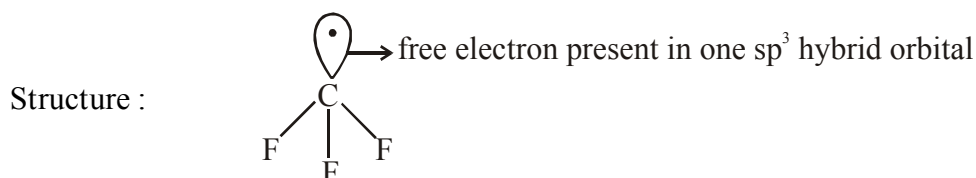
(3) ClO_3 :



(4) $\dot{\text{C}}\text{H}_3$:



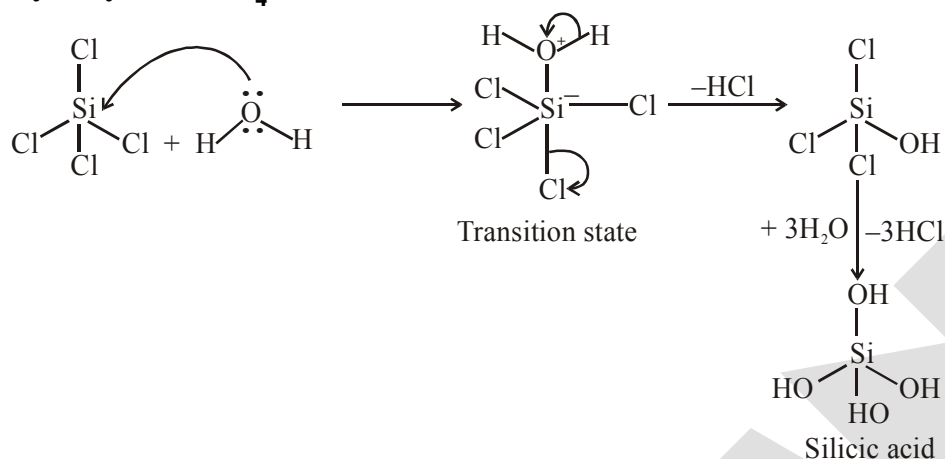
(5) $\dot{\text{C}}\text{F}_3$:



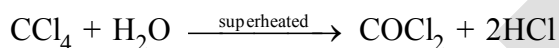
HYDROLYSIS :

In hydrolysis of covalent molecules the nucleophilic centre of molecule is replaced by OH^- group of water generally through nucleophilic substitution reaction.

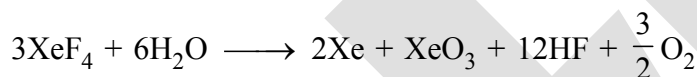
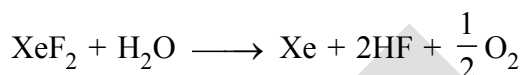
Ex. Hydrolysis of SiCl_4



Note : CCl_4 , NF_3 , is inert towards hydrolysis due to the absence of d orbital, but under drastic condition these molecules under goes hydrolysis.



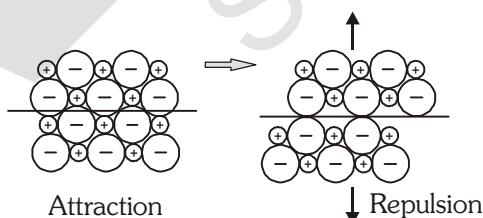
Note : Hydrolysis of XeF_2 & XeF_4 takes place through redox reaction.



IONIC COMPOUNDS

Properties of ionic compound

(a) Physical state : Ionic compounds are hard, crystalline and brittle due to strong electrostatic force of attraction. Brittleness \rightarrow {Same charged ions comes nearer. So they repel each other}



(b) Isomorphism : The phenomenon of different ionic compounds, having same crystal arrangement of ions is termed as isomorphism

Condition of Isomorphism :

- (i) Same charge on cation & anion between isomorphs
- (ii) Same radius ratio range of cation & anion between isomorphs
- (iii) Same number of water of crystallization between isomorphs

- Ex.** (i) $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ are isomorphous
 (ii) All alums are isomorphous

(c) Boiling point and melting point : Ionic compounds have high boiling point and melting point due to strong electrostatic force of attraction among oppositely charged ions.

(d) Conductivity : It depends on ionic mobility.

- (i) In solid state - No free ions - Bad conductor of electricity.
 (ii) In fused state or aqueous solution Due to free ions - Good conductor of electricity.

Conductivity order : Solid state < fused state < Aqueous solution

(e) Solubility :

Ionic compounds are more soluble in polar solvents and less soluble in non polar solvents.

- Solubility of ionic compounds in water mainly depends upon hydration energy & lattice energy.

Q. Why does the solubility of alkaline earth metal hydroxides in water increase down the group?

Ans. Among alkaline earth metal hydroxides, the anion being common the cationic radius will influence the lattice enthalpy. Since lattice enthalpy decreases much more than the hydration enthalpy with increasing ionic size, the solubility increases as we go down the group.

Q. Why does the solubility of alkaline earth metal carbonates and sulphates in water decrease down the group?

Ans. The size of anions being much larger compared to cations, the lattice enthalpy will remain almost constant within a particular group. Since the hydration enthalpies decrease down the group, solubility will decrease as found for alkaline earth metal carbonates and sulphates.

FAJAN'S RULE

Just as all the covalent bonds have some partial ionic character, the ionic bonds also have partial covalent character. The partial covalent character of ionic bonds was discussed by Fajans in terms of the following rules :

- The smaller the size of the cation and the larger the size of the anion, the greater the covalent character of an ionic bond.
- The greater the charge on the cation, the greater the covalent character of the ionic bond.
- For cations of the same size and charge, the one, with electronic configuration $(n-1)d^n ns^0$, typical of transition metals, is more polarising than the one with a noble gas configuration, $ns^2 np^6$, typical of alkali and alkaline earth metal cations.

- The cation polarises the anion, pulling the electronic charge toward itself and thereby increasing the electronic charge between the two. This is precisely what happens in a covalent bond, i.e., buildup of electron charge density between the nuclei. The polarising power of the cation, the polarisability of the anion and the extent of distortion (polarisation) of anion are the factors, which determine the per cent covalent character of the ionic bond.

⇒ Polarisation power of a cation is usually called ionic potential or charge density.

$$\text{Ionic potential } \phi (\text{phi}) = \frac{\text{Charge on cation}}{\text{Size of cation}}$$

APPLICATION OF THE CONCEPT OF POLARISATION :

- To compare the covalent and ionic character of molecule
- To compare the nature of oxide
- To compare the electrical conductivity of ionic compounds
- Tendency of the formation of complex compounds
- To compare the thermal stability of metal salts
- To compare the intensity of colour of compounds
- To compare the solubility of heavier metal halide in water.

MOLECULAR ORBITAL THEORY (MOT)

Given by Hunds & Mulliken

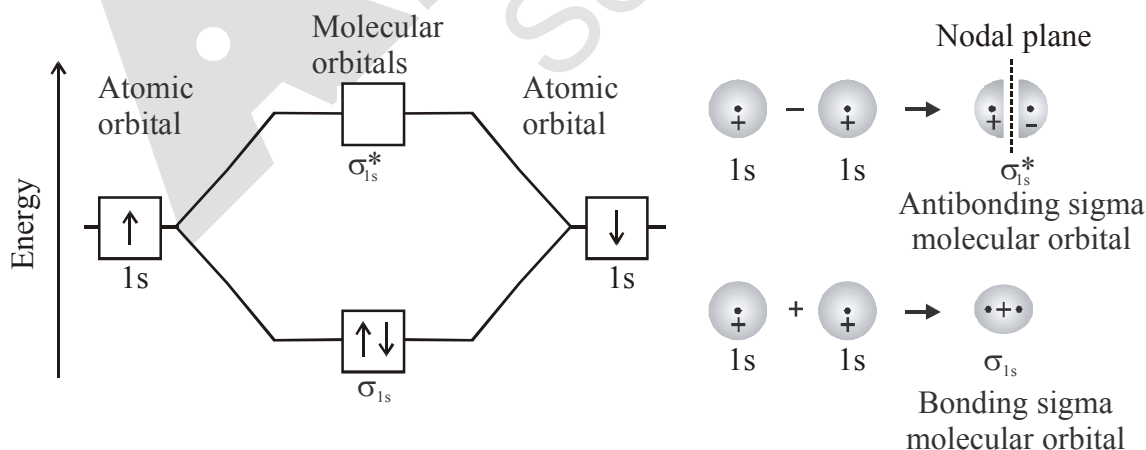
- Two atomic orbital come nearer & then overlap each other to form two molecular orbitals (MO)
- Combination of atomic orbital (AO) forms molecular orbital (MO)

Types of molecular orbitals

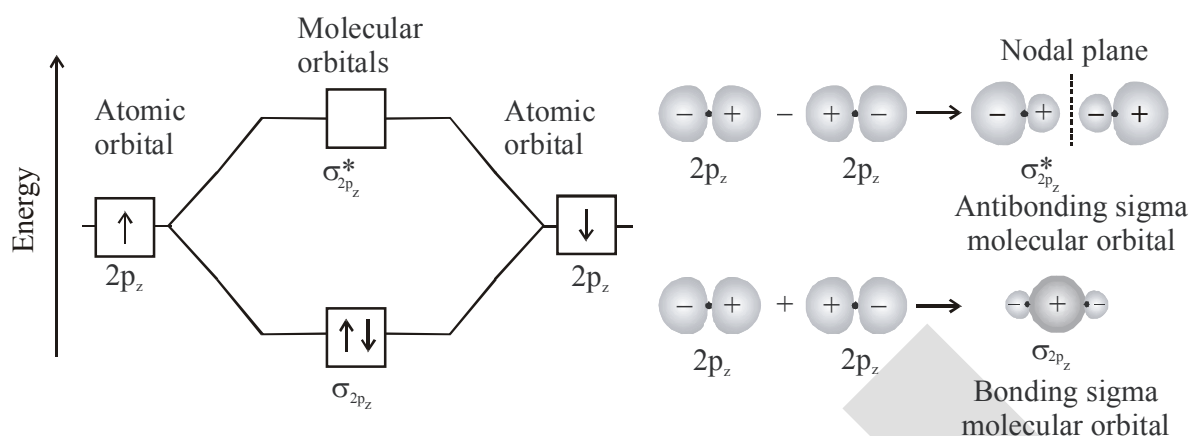
Molecular orbitals of diatomic molecules are designated as σ (sigma), π (pie), δ (delta) etc.

In this nomenclature, the **sigma (σ) molecular orbitals are symmetrical around the inter molecular axis (assumed to be z-axis) while pi (π) molecular orbitals are not symmetrical.**

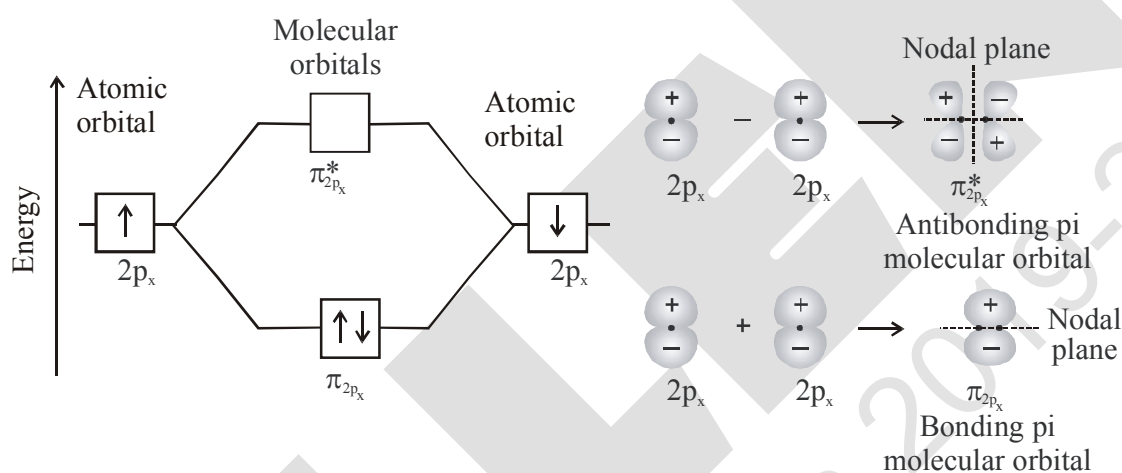
- s-s combination of orbitals



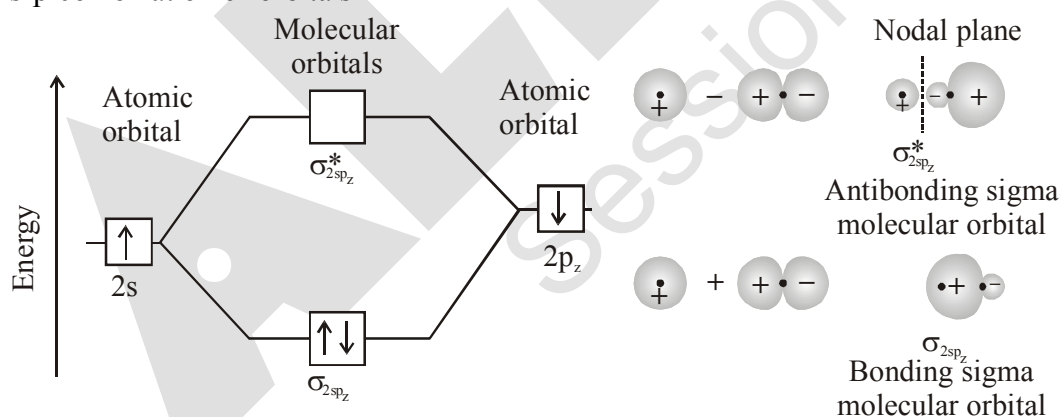
(2) p-p combination of orbitals(end to end overlap)



(3) p-p combination of orbitals (side by side overlap)



(4) s-p combination of orbitals



(c) Energy of BMO < Energy of ABMO.

(d) Molecular orbitals can be filled by electrons according to Aufbau, Hund's, Pauli's principle.

(e) Energy order of the molecular orbitals of homonuclear di-atomic molecules.

Note : Molecular orbital energy diagram for up to N₂ (molecule having ≤ 14 electrons)

$$\sigma_{1s} < \sigma_{1s}^* < \sigma_{2s} < \sigma_{2s}^* < \pi_{2p_x} = \pi_{2p_y} < \sigma_{2p_z} < \pi_{2p_x}^* = \pi_{2p_y}^* < \sigma_{2p_z}^*$$

Note : Molecular orbital energy diagram for O₂ and F₂ (molecule having > 14 electrons)

$$\sigma_{1s} < \sigma_{1s}^* ; < \sigma_{2s} < \sigma_{2s}^* < \sigma_{2p_z} < \pi_{2p_x} = \pi_{2p_y} < \pi_{2p_x}^* = \pi_{2p_y}^* < \sigma_{2p_z}^*$$

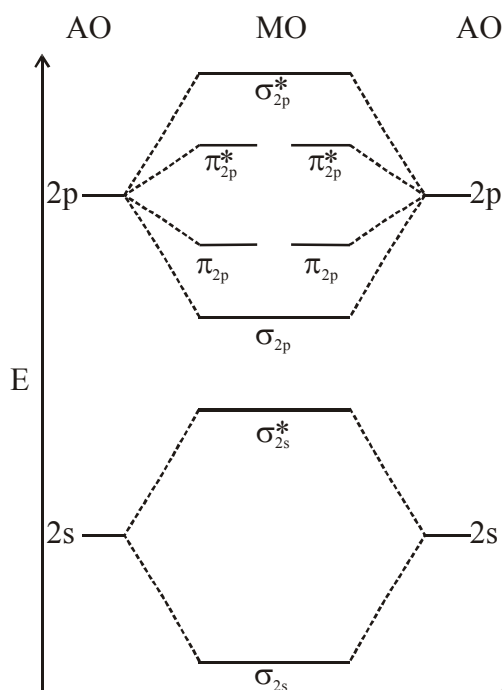
σ*, π* = antibonding molecular orbital

σ, π = bonding molecular orbital

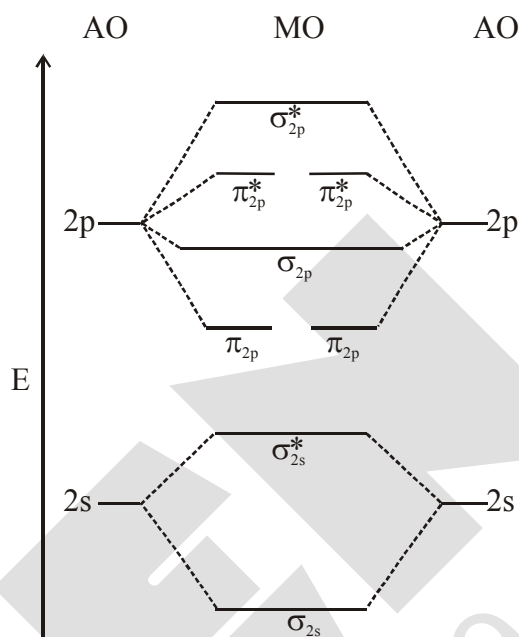
Ex. Why molecular orbitals have different order of energy in N_2 & O_2 ?

Sol. s-p mixing

Hint



The correct MO energy-level diagram when s-p mixing is not allowed.



The correct MO energy-level diagram when s-p mixing is allowed, the energies of the σ_{2p} and π_{2p} orbitals are reversed.

Bond Order

Bond order can be defined as :

$$\text{Bond order} = \frac{N_b - N_a}{2}$$

N_b = No. of electron in bonding MO's

N_a = No. of electron in antibonding MO's

- If bond order = 0, it means species does not exist.
- Bond order of 1, 2 & 3 corresponds to a single bond, double & triple bond respectively.
- Bond order \uparrow stability of molecule \uparrow bond length \downarrow

Magnetic behaviour

- If the molecule has one or more unpaired electron, it will be paramagnetic,
- If all the electrons are paired it will be diamagnetic.
- Magnetic strength can be calculated by using spin only formula of magnetic moment (μ).
- $\mu = \sqrt{n(n+2)}$ B.M. (where n = number of unpaired electron)

Ex. H_2 = Configuration : $\sigma_{(1s)}^2, \sigma_{(1s)}^{*0}$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{2 - 0}{2} = 1,$$

Hence H – H (diamagnetic)

EXERCISE # (O-1)

WEAK FORCES

- Statement-1 :** The melting point of noble gases increases as its atomic mass increases.
Statement-2 : Instantaneous dipole induced dipole attraction increases with increase in atomic mass of noble gases.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1
 (C) Statement-1 is true, statement-2 is false.
 (D) Statement-1 is false, statement-2 is true.
- The critical temperature of water is higher than that of O_2 because the H_2O molecule has :

(A) fewer electrons than O_2 (B) two ionic bonds
 (C) V-shape (D) dipole moment
- Which of the following boiling point order is correct -

(A) $He > T_2 > D_2$ (B) $He < T_2 < D_2$ (C) $T_2 > He > D_2$ (D) $He < D_2 < T_2$
- Which is the incorrect match for the energy distance function for following interaction -

(A) Debye force : r^{-6} (B) Ion-induced dipole interaction : r^{-2}
 (C) London force : r^{-6} (D) Keesom force : r^{-3}
- Identify the incorrect order of boiling point in the following pair.

(A) $B(OH)_3 < B(OMe)_3$ (B) $NF_3 < N(CH_3)_3$
 (C) $BF_3 < B(CH_3)_3$ (D) $C_2H_6 < C_2F_6$

BENT'S RULE AND DRAGO'S

- C-H bond distance is the longest in:

(A) C_2H_2 (B) C_2H_4 (C) C_2H_6 (D) $C_2H_2Br_2$
- The bond angle and hybridization in ether (CH_3OCH_3) is :

(A) $106^\circ 51'$, sp^3 (B) $104^\circ 31'$, sp^3 (C) 110° , sp^3 (D) None of these
- Which of the following has been arranged in order of decreasing bond length ?

(A) $P-O > Cl-O > S-O$ (B) $P-O > S-O > Cl-O$
 (C) $S-O > Cl-O > P-O$ (D) $Cl-O > S-O > P-O$
- Which is correct statement ?

As the s-character of a hybrid orbital decreases

(I) The bond angle decreases (II) The bond strength increases
 (III) The bond length increases (IV) Size of orbital increases

(A) (I), (III) and (IV) (B) (II), (III) and (IV)
 (C) (I) and (II) (D) All are correct
- Among the following, the correct statement is :

(A) Between NH_3 and PH_3 , NH_3 is a better electron donor because the lone pair of electrons occupies spherical 's' orbital and is less directional
 (B) Between NH_3 and PH_3 , PH_3 is a better electron donor because the lone pair of electrons occupies sp^3 orbital and is more directional
 (C) Between NH_3 and PH_3 , NH_3 is a better electron donor because the lone pair of electrons occupies sp^3 orbital and is more directional
 (D) Between NH_3 and PH_3 , PH_3 is a better electron donor because the lone pair of electrons occupies spherical 's' orbital and is less directional

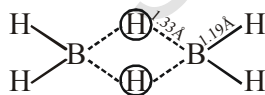
11. In which of the following molecule C—C bond length will be highest ?
 (A) $\text{CF}_3 - \text{CF}_3$ (B) $\text{F}_2\text{CH} - \text{CHF}_2$ (C) $\text{FCH}_2 - \text{CH}_2\text{F}$ (D) $\text{CH}_3 - \text{CF}_3$
12. In BClBrI molecule the maximum % s-character provided from the central atom is in bond :
 (A) B—I (B) B—Cl (C) B—Br (D) Can not predict
13. Find out the % p-character in the orbital occupied by lone pairs in H_2O .
 $[\widehat{\text{HOH}} = 104.5^\circ \text{ and } \cos(104.5) = -0.25]$
 (A) 80 % (B) 20 % (C) 70 % (D) 75 %
14. Which of the following order is correct for increasing p-character in orbital used for bonding by central atom
 (A) $\text{SiH}_4 > \text{CH}_4$ (B) $\text{H}_2\text{S} > \text{H}_2\text{O}$ (C) $\text{PH}_4^+ > \text{PH}_3$ (D) $\text{NH}_3 > \text{PH}_3$

BACK BONDING

15. Boron forms BX_3 type of halides. The correct increasing order of Lewis-acid strength of these halides is
 (A) $\text{BF}_3 > \text{BCl}_3 > \text{BBr}_3 > \text{BI}_3$ (B) $\text{BI}_3 > \text{BBr}_3 > \text{BCl}_3 > \text{BF}_3$
 (C) $\text{BF}_3 > \text{BI}_3 > \text{BCl}_3 > \text{BBr}_3$ (D) $\text{BF}_3 > \text{BCl}_3 > \text{BI}_3 > \text{BBr}_3$
16. Select species which is planar at nitrogen :
 (A) $(\text{CH}_3)_3\text{N}$ (B) $(\text{SiH}_3)_3\text{N}$ (C) NF_3 (D) NH_3
17. Type of back bonding in $(\text{SiH}_3)_2\text{O}$ is :
 (A) $p\pi - d\pi$ (B) $p\pi - p\pi$ (C) $d\pi - d\pi$ (D) None of these

MULTICENTERED BOND

18. The type of overlap in the bridge bond existing in $\text{Al}_2(\text{CH}_3)_6$ is :-
 (A) $sp^3-sp^3d-sp^3$ (B) $sp^3-sp^2-sp^3$ (C) sp^3-s-sp^3 (D) $sp^3-sp^3-sp^3$
19. Which one of the following statement is not true regarding diborane?
 (A) It has two bridging hydrogens and four perpendicular to the rest.
 (B) When methylated, the product is $\text{Me}_4\text{B}_2\text{H}_2$
 (C) The bridging hydrogens are in a plane perpendicular to the rest.
 (D) All the B—H bond distances are equal.
20. The molecular shape of diborane, is shown:



Consider the following statements for diborane :

- (1) Boron is approximately sp^3 hybridised
 (2) B—H—B angle is 180°
 (3) There are two terminal B—H bonds for each boron atom
 (4) There are only 12 bonding electrons available

Of these statements:

- (A) 1, 3 and 4 are correct (B) 1, 2 and 3 are correct
 (C) 2, 3 and 4 are correct (D) 1, 2 and 4 are correct

SILICATE

21. The number of corners or O-atoms shared per tetrahedron for pyroxene chain silicate is -
 (A) 3 (B) 2 (C) 2.5 (D) 1
22. The mineral $\text{Na}_2\text{Fe}_3^{\text{II}}\text{Fe}_2^{\text{III}}[\text{Si}_8\text{O}_{22}](\text{OH})_2$ (chrocidolite) is a :
 (A) Pyroxene chain silicate (B) Sheet silicate
 (C) Amphiboles chain silicate (D) 3D-silicate
23. The silicate anion in the mineral kunoite is a chain of three SiO_4 tetrahedral those share corners with adjacent tetrahedral. The mineral also contains Ca^{2+} ions, Cu^{2+} ions, and water molecules in a 1:1:1 ratio mineral is represented as :
 (A) $\text{CaCuSi}_3\text{O}_{10} \cdot \text{H}_2\text{O}$ (B) $\text{CaCuSi}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$
 (C) $\text{Ca}_2\text{Cu}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$ (D) none of these

ODD ELECTRON SPECIES

24. Hybridisation related to NO_2 molecule is -
 (A) sp^3 (B) sp
 (C) sp^3d (D) sp^2
25. In which of the following processes, the magnetic behaviour of the species is changed :-
 (A) $2\dot{\text{C}}\text{H}_3 \longrightarrow \text{C}_2\text{H}_6$ (B) $2\text{NO}_2 \longrightarrow \text{N}_2\text{O}_4$
 (C) $2\text{ClO}_3 \longrightarrow \text{Cl}_2\text{O}_6$ (D) All of these

HYDROLYSIS

26. Which of the following statement is correct ?
 (A) BCl_3 is not hydrolysed while SiCl_4 can be hydrolysed
 (B) CCl_4 is hydrolysed under ordinary condition
 (C) XeF_2 produces $\text{Xe}(\text{OH})_2$ on hydrolysis
 (D) hydrolysis of XeF_2 is a redox reaction
27. **Statement-1** : Between SiCl_4 and CCl_4 only SiCl_4 reacts with water at room temperature.
Statement-2 : SiCl_4 is ionic and CCl_4 is covalent.
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1
 (C) Statement-1 is true, statement-2 is false.
 (D) Statement-1 is false, statement-2 is true.

28. **Statement-1** : PCl_3 on hydrolysis gives $\text{OH}-\overset{\text{O}}{\underset{\text{H}}{\text{P}}}-\text{OH}$ and $\text{OH}-\underset{\text{OH}}{\text{P}}-\text{OH}$

Statement-2 : H_3PO_3 exists in two tautomeric forms : $\text{OH}-\underset{\text{OH}}{\text{P}}-\text{OH} \rightleftharpoons \text{OH}-\overset{\text{H}}{\underset{\text{O}}{\text{P}}}-\text{OH}$

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1
 (C) Statement-1 is true, statement-2 is false.
 (D) Statement-1 is false, statement-2 is true.

MOLECULE DOES NOT EXIST

29. Which of the following molecule does not exist.

- (A) PH_5 (B) NCl_3 (C) NOF_3 (D) XeF_5^-

30. Select non existing specie

- (A) PH_3 (B) PH_4^+
 (C) $[\text{PF}_6]^-$ (D) None of these

INERT PAIR EFFECT

31. **Statement-1** : Boron does not show univalent nature but unipositive nature of thallium is quite stable.

Statement-2 : Inert pair effect predominates in thallium.

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1
 (C) Statement-1 is true, statement-2 is false.
 (D) Statement-1 is false, statement-2 is true.

32. **Statement-1** : PbI_4 doesn't exist and converts into PbI_2 and I_2 spontaneously at room temperature but PbCl_4 needs heating to convert into PbCl_2 and Cl_2 .

Statement-2 : Pb^{2+} is more stable than Pb^{4+} due to inert pair effect.

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1
 (C) Statement-1 is true, statement-2 is false.
 (D) Statement-1 is false, statement-2 is true.

IONIC COMPOUND

33. The dissolution of ionic compounds involves :
 (A) Evolution of heat (B) Weakening of attractive forces
 (C) Dissociation into ions (D) All of these
34. Select correct order out of given options :
 (A) $\text{BeCO}_3 < \text{BaCO}_3$: Covalent character (B) $\text{BeO} > \text{SrO}$: lattice energy
 (C) $\text{Be}^{2+} < \text{Li}^+$: Hydration energy (D) $\text{Be}^{2+}(\text{aq.}) > \text{Li}^+(\text{aq.})$: Ionic mobility
35. The polarizability of the following ions is/are in the order of
 (A) $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$ (B) $\text{I}^- > \text{Br}^- > \text{F}^- > \text{Cl}^-$
 (C) $\text{I}^- < \text{Br}^- < \text{Cl}^- < \text{F}^-$ (D) $\text{I}^- < \text{Br}^- < \text{F}^- < \text{Cl}^-$
36. Which of the following equilibria would have the highest value of K_p at a common temperature?
 (A) $\text{MgCO}_3 \rightleftharpoons \text{MgO} + \text{CO}_2$ (B) $\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$
 (C) $\text{SrCO}_3 \rightleftharpoons \text{SrO} + \text{CO}_2$ (D) $\text{BaCO}_3 \rightleftharpoons \text{BaO} + \text{CO}_2$
37. Which of the following set of characteristics lead to the increase in solubility of ionic substances?
 (A) High dipole moment, strong attraction by an ion towards solvent and large solvation energy
 (B) Low dipole moment, weak attraction by an ion towards solvent and high solvation energy
 (C) High dipole moment, strong attraction by an ion towards solvent and low solvation energy
 (D) High dipole moment, weak attraction by an ion towards solvent and large solvation energy
38. The solubility of anhydrous AlCl_3 and hydrated AlCl_3 in diethyl ether are S_1 and S_2 respectively. Then
 (A) $S_1 = S_2$ (B) $S_1 > S_2$ (C) $S_1 < S_2$ (D) $S_1 < S_2$ but not $S_1 = S_2$
39. **Statement-1** : Among alkali metal cations, $\text{Li}^+(\text{aq.})$ has highest electrical conductance.
Statement-2 : $\text{Li}^+(\text{aq.})$ is largest alkali metal cation because of greater degree of hydration.
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1
 (C) Statement-1 is true, statement-2 is false.
 (D) Statement-1 is false, statement-2 is true.
40. **Statement-1** : $\text{Al}(\text{OH})_3$ is amphoteric in nature.
Statement-2 : Al-O and O-H bonds can be broken with equal ease in $\text{Al}(\text{OH})_3$.
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1
 (C) Statement-1 is true, statement-2 is false.
 (D) Statement-1 is false, statement-2 is true.

MOLECULAR ORBITAL THEORY

41. The bond energy order of He_2^+ and HeH^+ is
 (A) $\text{He}_2^+ > \text{HeH}^+$ (B) $\text{HeH}^+ = \text{He}_2^+$ (C) $\text{HeH}^+ > \text{He}_2^+$ (D) Can't be predicted
42. Among KO_2 , AlO_2^- , BaO_2 and NO_2^+ unpaired electron is present in :
 (A) KO_2 only (B) NO_2^+ and BaO_2 (C) KO_2 and AlO_2^- (D) BaO_2 only
43. During the formation of a molecular orbital from atomic orbitals, probability of electron density is
 (A) minimum in the nodal plane (B) maximum in the nodal plane
 (C) zero in the nodal plane (D) zero on the surface of the lobe

44. Pick out the **incorrect** statement ?
 (A) N_2 has greater dissociation energy than N_2^+
 (B) O_2 has lower dissociation energy than O_2^+
 (C) Bond length in N_2^+ is less than N_2
 (D) Bond length in NO^+ is less than in NO
45. A simplified application of MO theory to the hypothetical molecule 'OF' would give its bond order as :
 (A) 2 (B) 1.5 (C) 1.0 (D) 0.5
46. Which of the following is true ?
 (A) With increasing Bond order, Bond length decreases & Bond energy increases
 (B) With increasing Bond order, Bond length increases & Bond energy decreases
 (C) With increasing Bond order, Bond length decreases & Bond energy decreases
 (D) With increasing Bond order, Bond length increases & Bond energy increases
47. Which of the following has fractional bond order :
 (A) O_2^{2+} (B) O_2^{2-} (C) F_2^{2-} (D) H_2^-
48. **Statement-1:** H_2 molecule is more stable than He-H molecule.
Statement-2 : The antibonding electron in He-H molecule decreases the bond order and there by the stability.
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1
 (C) Statement-1 is true, statement-2 is false.
 (D) Statement-1 is false, statement-2 is true.
49. **Statement-1 :** Super oxide ion is paramagnetic whereas peroxide ion is diamagnetic.
Statement-2 : Super oxide ion has one unpaired electron whereas peroxide ion has no unpaired electron.
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1
 (C) Statement-1 is true, statement-2 is false.
 (D) Statement-1 is false, statement-2 is true.
50. **Statement-1:** π_b and π^* orbitals obtained from 2p orbital are lying in the same plane.
Statement-2 : Bonding M.O's are formed by constructive interference while antibonding M.O's are formed by destructive interference.
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1
 (C) Statement-1 is true, statement-2 is false.
 (D) Statement-1 is false, statement-2 is true.

EXERCISE # (O-2)

WEAK FORCES

- Which of the following factors are responsible for origination of vander Waals forces ?
 (A) Instantaneous dipole-induced dipole interaction
 (B) Dipole-induced dipole interaction
 (C) Dipole-dipole interaction
 (D) Size of molecule
- Which of the following are true ?
 (A) Vander Waals forces are responsible for the formation of molecular crystals
 (B) Branching lowers the boiling points of isomeric organic compounds due to decrease in Vander Waals forces of attraction
 (C) In graphite, vander Waals forces act between the carbon layers
 (D) In diamond, vander Waals forces act between the carbon layers

BENT'S AND DRAGO'S RULE

- Select the correct statement for following molecules :
 (I) $\text{PF}_2(\text{CH}_3)_3$; (II) $\text{PF}_2(\text{CF}_3)_3$
 (A) Both have trigonal bipyramidal structure with respect to P.
 (B) P-F bond length is longer in $\text{PF}_2(\text{CH}_3)_3$ than in $\text{PF}_2(\text{CF}_3)_3$
 (C) F-atoms occupy axial position in both
 (D) P-F bond length is lower in $\text{PF}_2(\text{CH}_3)_3$ than in $\text{PF}_2(\text{CF}_3)_3$

BACK BONDING

- Molecules in which bond angle is changed due to back bonding w.r.t B/O/N.
 (A) H_3BO_3 (B) $\text{B}(\text{OMe})_3$ (C) BF_3 (D) $\text{N}(\text{SiH}_3)_3$
- $3d\pi-2p\pi$ type back bonding is observed in :
 (A) $\text{N}(\text{SiH}_3)_3$ (B) CCl_3 (C) $\text{S}(\text{CH}_3)_2$ (D) BCl_3

MULTICENTERED BOND

- No X-X bond exists in which of the following compounds having general form of X_2H_6 ?
 (A) B_2H_6 (B) C_2H_6 (C) Al_2H_6 (D) Si_2H_6
- Three centre - two electron bonds exist in :
 (A) B_2H_6 (B) $\text{Al}_2(\text{CH}_3)_6$ (C) $\text{BeH}_2(\text{s})$ (D) $\text{BeCl}_2(\text{s})$
- Select correct statement about B_2H_6
 (A) Bridging groups are electron-deficient with 12 valence electrons
 (B) It has $2c - 2e$ B-H bonds
 (C) It has $3c - 2e$ B-H-B bonds
 (D) It has $3c - 4e$ B-H-B bonds

SILICATE

- In which of the following cases the number of corner shared per tetrahedron is '2' -
 (A) Pyroxene chain silicate (B) Amphibole chain silicate
 (C) 5-membered cyclic silicate (D) None of these

ODD ELECTRON SPECIES

10. Select correct about NO_2 :
 (A) It is odd electron specie (B) N–O bond order = 1.5
 (C) Paramagnetic specie (D) Isoelectronic with CO_2
11. The number of specie(s) which are not perfectly planar.
 (A) $\dot{\text{C}}\text{H}_3$ (B) $\dot{\text{C}}\text{F}_3$ (C) $\dot{\text{C}}\text{HF}_2$ (D) $\dot{\text{C}}\text{H}_2\text{F}$
12. Which of the following statement is **CORRECT** :-
 (A) The free electron of ClO_3 molecule is present in d-orbital of Cl-atom
 (B) The free electron of $\dot{\text{C}}\text{F}_3$ is present in sp^3 hybrid orbital
 (C) NO is polar
 (D) The free electron of ClO_2 molecule is present in d-orbital of Cl-atom
13. Which of the following statement(s) is / are **INCORRECT** for
 $\dot{\text{C}}\text{H}_3 = \text{X}$ and $\dot{\text{C}}\text{F}_3 = \text{Y}$
 (A) When X dimerises bond angle decreases
 (B) When X dimerises bond angle increases
 (C) In X–Y molecule C–C bond length less than that in Y–Y molecule
 (D) Bond angle in Y is less than X

HYDROLYSIS

14. Which of the following halide(s) cannot be hydrolysed at room temperature
 (A) SeF_6 (B) SF_6 (C) CCl_4 (D) NF_3
15. Which of the following statement is/are **INCORRECT** ?
 (A) P_4S_{10} gives rise to H_2S gas on hydrolysis
 (B) PCl_5 produces POCl_3 on partial hydrolysis
 (C) H_2SO_5 gives rise to H_2SO_3 on hydrolysis
 (D) d-orbital participates in the hydrolysis of SF_6 at room temperature

MOLECULE DOES NOT EXIST

16. Which of the following do/does not exist ?
 (A) SH_6 (B) HFO_4 (C) FeI_3 (D) HClO_3
17. Which of the following molecule(s) exist-
 (A) SF_6 (B) PH_5 (C) PH_3 (D) PCl_5

INERT PAIR EFFECT

18. Which of the following have $(18 + 2)$ electron configuration ?
 (A) Pb^{2+} (B) Cd^{2+} (C) Bi^{3+} (D) SO_4^{2-}

19. Which of following stability order is/are correct due to inert pair effect.

- (A) $\text{Hg} > \text{Hg}^{2+}$ (B) $\text{Bi}^{3+} < \text{Bi}^{5+}$ (C) $\text{Pb}^{2+} > \text{Pb}^{4+}$ (D) $\text{Fe}^{2+} < \text{Fe}^{3+}$

IONIC COMPOUND

20. Choose the correct order(s) for the given properties.

- (A) $\text{MgSO}_4 < \text{SrSO}_4 < \text{BaSO}_4$: Thermal stability order
 (B) $\text{BeC}_2\text{O}_4 < \text{CaC}_2\text{O}_4 < \text{BaC}_2\text{O}_4$: Solubility in water
 (C) $\text{LiCl} > \text{NaCl} > \text{KCl}$: Melting point order
 (D) $\text{BeF}_2 > \text{CaF}_2 > \text{SrF}_2$: Covalent character order

21. Polarization may be called the distortion of the shape of an anion by an adjacently placed cation. Which of the following statements is/are incorrect :

- (A) Minimum polarization is brought about by a cation of low radius
 (B) A large cation is likely to bring about a large degree of polarization
 (C) Maximum polarization is brought about by a cation of high charge
 (D) A small anion is likely to undergo a large degree of polarization

22. Most ionic compounds have :

- (A) high melting points and low boiling points
 (B) high melting points and nondirectional bonds
 (C) high solubilities in polar solvents and low solubilities in nonpolar solvents
 (D) three-dimensional network structures, and are good conductors of electricity in the molten state

23. Choose the correct order for the given properties.

- (A) $\text{NaF} < \text{MgF}_2 < \text{AlF}_3$: covalent character order.
 (B) $\text{NaF} < \text{MgF}_2 < \text{AlF}_3$: melting point order
 (C) $\text{NaF} < \text{MgF}_2 < \text{AlF}_3$: lattice energy order
 (D) $\text{NaF} > \text{MgF}_2 > \text{AlF}_3$: order of polarising power of cation.

MOLECULAR ORBITAL THEORY

24. Which of the following have identical bond order ?

- (A) O_2^{2+} (B) NO^+ (C) CN^- (D) CN^+

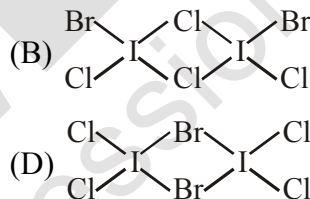
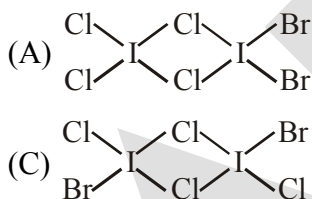
25. Which of the following statement is/are correct

- (A) The peroxide ion has a bond order of 1 while the oxygen molecule has a bond order of 2
 (B) The peroxide ion has a weaker bond than the dioxygen molecule has.
 (C) The peroxide ion as well as the dioxygen molecules are paramagnetic
 (D) The bond length of the peroxide ion is greater than that of the dioxygen molecule

26. Which of the following statements are true for these given species : N_2 , CO , CN^- and NO^+ .
- (A) All species are paramagnetic (B) The species are isoelectronic
(C) All the species have dipole moment (D) All the species are linear
27. Which of the following have unpaired electron(s)
- (A) O_2^+ (B) O_2^- (C) NO (D) H_2^+
28. Which of the following is/are paramagnetic ?
- (A) B_2 (B) O_2 (C) N_2 (D) He_2
29. Which of the following species have a bond order of 3 ?
- (A) CO (B) CN^- (C) NO^+ (D) O_2^+
30. Which of the following is/are correct ?
- (A) During N_2^+ formation, one electron is removed from the bonding molecular orbitals
(B) During O_2^+ formation, one electron is removed from the antibonding molecular orbitals
(C) During O_2^- formation, one electron is added to the bonding molecular orbitals
(D) During CN^- formation, one electron is added to the bonding molecular orbitals

MISCELLANEOUS

31. Rotation around the bond (between the underlined atoms) is restricted in :
- (A) \underline{C}_2H_4 (B) $H_2\underline{O}_2$ (C) \underline{C}_2H_2 (D) \underline{C}_2H_6
32. The experimental result says that two iodine atoms are in different environments and predict the all possible incorrect arrangement for $I_2Cl_4Br_2$.



EXERCISE # (S-1)

- The number of corner of O-atom shared per tetrahedron in 2D-silicate is
- Find the number of angles less than 120° in PH_2F_3 .
- Find the number of molecules which are not having 3c-2e bond from the following.
 $\text{Al}_2(\text{CH}_3)_6$, Si_2H_6 , B_2H_6 , C_2H_6 , Si_2Cl_6 , Al_2Cl_6
- Find the ratio of π -electrons in the C_2 -molecule with that of B_2 molecule according to M.O.T.
- In which of the following silicates structure, the number of corner/oxygen atoms shared per tetrahedron is '2'.
 Pyrosilicate, pyroxene chain silicate,
 2D-silicate, 3D-silicate, 4-membered cyclic silicate
- The total number of bonding and antibonding electrons in O_2^+ are "....." and "....." respectively.
[If the answer is 14 and 7, then represent as 147]
- Find the total number of following molecule(s) which have all bond lengths are same.
 XeF_4 , SF_4 , SH_2 , NO_3^- , SiF_4 , ClF_3 , PF_2Cl_3 , XeO_3F_2
- Among the following total number of planar molecules is / are
 Cl_2O , $\text{P}(\text{CH}_3)_3$, $\text{N}(\text{CH}_3)_3$, ClO_2 , $\cdot\text{CH}_3$, NCl_3
- Calculate the value of "n" in $\text{Zn}_n\text{Ca}_2(\text{Si}_3\text{O}_{10}) \cdot 2\text{H}_2\text{O}$
- How many compound(s) gives diprotic acid on hydrolysis?
 SO_2Cl_2 , SOCl_2 , POCl_3 , XeF_2 , N_2O_5 , P_4O_6 , SF_4 , BCl_3

EXERCISE # (S-2)

Comprehension # 1 (1 to 3 Questions)

B is the first element of IIIrd group. It forms a number of electron deficient halides and hydrides. Among the hydrides diborane is an important compound.

- Which of the following halide is the strongest Lewis acid?
(A) BF_3 (B) BCl_3 (C) BBr_3 (D) BI_3
- Which of the following compounds has $2p\pi - 2p\pi$ bond?
(A) BF_3 (B) BCl_3 (C) BBr_3 (D) BI_3
- In B_2H_6 number of $3c - 2e$ bonds is/are
(A) 1 (B) 2 (C) 3 (D) None

Comprehension # 2 (4 to 6 Questions)

Molecular orbital theory is based on linear combination of atomic orbitals (LCAO). According to LCAO when respective atomic orbitals of the atoms interact, they undergoes constructive and destructive interference giving two types of molecular orbital i.e. bonding and antibonding molecular orbitals respectively.

- Which of the following specie is paramagnetic?
(A) NO^- (B) O_2^{2-} (C) CN^- (D) CO
- Bond order of Be_2 is :
(A) 1 (B) 2 (C) 3 (D) 0
- Number of anti bonding electrons in N_2 is :
(A) 4 (B) 10 (C) 12 (D) 14

Comprehension # 3 (7 to 8 Questions)

Polarisation of anion in ionic compounds play an important role to influence the various physical and chemical properties of ionic compound.

- Amongst LiCl , RbCl , BeCl_2 and MgCl_2 the compounds with the greatest and the least ionic character, respectively are :
(A) LiCl and RbCl (B) RbCl and BeCl_2 (C) RbCl and MgCl_2 (D) MgCl_2 and BeCl_2
- Compound with maximum ionic character is formed from :
(A) Na and Cl (B) Cs and F (C) Cs and I (D) Na and F

Comprehension # 4 (9 to 10 Questions)

"Hydrolysis is defined as the reaction of water with any substance"

- Choose the correct order of ease of hydrolysis -
(A) $\text{MgCl}_2 > \text{AlCl}_3$ (B) $\text{SF}_6 < \text{SeF}_6$ (C) $\text{SnCl}_2 > \text{SnCl}_4$ (D) None
- Which of the following oxyacids are formed during the stepwise hydrolysis of P_4O_{10}
(A) tetrametaphosphoric acid (B) tetrapolyphosphoric acid
(C) pyrophosphoric acid (D) All of these

MATCHING LIST

11. Match list I with list II and select the correct answer:

List I (species)				List II (O-N-O angle)			
(P)	NO_2^+			(1)	180°		
(Q)	NO_2			(2)	134°		
(R)	NO_2^-			(3)	120°		
(S)	NO_3^-			(4)	115°		
				(5)	109°		

	P	Q	R	S		P	Q	R	S
(A)	5	4	3	2	(B)	5	2	4	3
(C)	1	2	4	3	(D)	1	4	3	2

12. Match list I with list II and select the correct answer:

List-I (Molecule / Species)				List-II (Unpaired electron resides in)			
(P)	NO_2			(1)	d-orbital		
(Q)	ClO_2			(2)	sp^2 -orbital		
(R)	ClO_3			(3)	sp^3 -orbital		
(S)	$\cdot\text{CH}_3$			(4)	p-orbital		

Code :

	P	Q	R	S		P	Q	R	S
(A)	2	4	1	3	(B)	2	1	3	4
(C)	1	4	2	3	(D)	3	1	2	4

13. Match list I with list II and select the correct answer:

List-I (Process)				List-II (Operating interaction involved)			
(P)	Clathrate compound of Xe in ice			(1)	Ion - Dipole		
(Q)	Liquation of Xe gas			(2)	Dipole - Dipole		
(R)	Liquation of HCl gas			(3)	Dipole - Induced dipole		
(S)	Hydration of Na^+			(4)	London forces		

Code :

	P	Q	R	S		P	Q	R	S
(A)	1	3	4	2	(B)	3	4	1	2
(C)	3	4	2	1	(D)	1	3	2	4

MATRIX MATCH

14. Match the column

Column-I (Compounds given)	Column-II (Characteristics associated with given compounds)
(A) BeCl_2	(P) Undergoes partial hydrolysis
(B) SiF_4	(Q) All possible bond angles are identical
(C) SO_2Cl_2	(R) Hydrolysed product of the attacking site is electron deficient and finally produces polymerised product
(D) BF_3	(S) Maximum number of atoms present in one plane is three

15. Match the column

Column-I
(Molecules)

- (A) CH_4
(B) CH_2F_2
(C) CHF_3
(D) CF_4

Column-I

(Characteristics given among the molecules of column-I)

- (P) Molecule is having perfect tetrahedral shape
(Q) C-F bond has maximum p-character
(R) C-H bond has maximum s-character
(S) Molecule is having maximum number of equal angles
(T) Molecule has lowest bond angle

16. Match the column

Column-I
Processes

- (A) $\text{N}_2^+ \longrightarrow \text{N}_2$
(B) $\text{Zn}^{2+} \longrightarrow \text{Zn}$
(C) $\text{O}_2^{2-} \longrightarrow 2\text{O}^{2-}$
(D) $\text{C}_2^{2-} \longrightarrow \text{C}_2$

Column-II

Correct characteristics

- (P) Magnetic moment gets changed
(Q) The process is associated with two electronic change
(R) Magnetic behaviour gets changed
(S) Electron(s) associated in the process enter(s) into π_{2p}^* orbital
(T) Electron(s) associated in the process involve(s) σ_{2p} orbital

Answer Q.17 to Q.19 by appropriately matching the information given in the three columns of the following table

Molecular Orbital	Number of nodal plane	Symmetry of Molecular Orbital
(1) σ_s	(P) 3	(I) BMO, gerade
(2) π_p	(Q) 2	(II) ABMO, ungerade
(3) $\sigma_{p_z}^*$	(R) 1	(III) BMO, ungerade
(4) δ^*	(S) 0	(IV) ABMO, gerade

17. Which of the following matching is **INCORRECT**.

- (A) (1), S, I (B) (2), R, I (C) (3), R, II (D) (4), P, II

18. How many orbitals are occupied with set (1)(S)(I) in F_2

- (A) 0 (B) 1 (C) 2 (D) 3

19. If z axis is the molecular axis then **CORRECT** matching for $d_{xy} + d_{xy}$ orbital is 4, P, II for the subtraction of wave function.

Which of the following matching is **CORRECT** for the addition of wave function for same combination of orbitals.

- (A) P, IV (B) P, III (C) Q, II (D) Q, I

EXERCISE # J-MAIN

- The bond order in NO is 2.5 while that in NO^+ is 3. Which of the following statement is true for these two species ? [AIEEE-2004]
 - (1) Bond length in NO^+ is equal to that NO
 - (2) Bond length in NO is greater than NO^+
 - (3) Bond length in NO^+ is greater than NO
 - (4) Bond length is unpredictable
- The states of hybridization of boron and oxygen atoms in boric acid (H_3BO_3) are respectively [AIEEE-2004]
 - (1) sp^3 and sp^2
 - (2) sp^2 and sp^3
 - (3) sp^2 and sp^2
 - (4) sp^3 and sp^3
- The maximum number of 90° angles between bond pair-bond pair of electrons is observed in :- [AIEEE-2004]
 - (1) dsp^2 hybridization
 - (2) sp^3d hybridization
 - (3) dsp^3 hybridization
 - (4) sp^3d^2 hybridization
- Which one of the following specie is diamagnetic in nature ? [AIEEE-2005]
 - (1) He_2^+
 - (2) H_2
 - (3) H_2^+
 - (4) H_2^-
- Which of the following molecule/ion does not contain unpaired electrons? [AIEEE-2006]
 - (1) N_2^+
 - (2) O_2
 - (3) O_2^{2-}
 - (4) B_2
- Among the following mixtures, dipole-dipole as the major interaction, is present in [AIEEE-2006]
 - (1) KCl and water
 - (2) benzene and carbon tetrachloride
 - (3) benzene and ethanol
 - (4) acetonitrile and acetone
- A metal, M forms chlorides in its +2 and +4 oxidation states. Which of the following statement about these chlorides is correct ? [AIEEE-2006]
 - (1) MCl_2 is more ionic than MCl_4
 - (2) MCl_2 is more easily hydrolysed than MCl_4
 - (3) MCl_2 is more volatile than MCl_4
 - (4) MCl_2 is more soluble in anhydrous ethanol than MCl_4
- The decreasing values of bond angles from NH_3 (106°) to SbH_3 (91°) down group-15 of the periodic table is due to [AIEEE-2006]
 - (1) decreasing lp – bp repulsion
 - (2) increasing electronegativity
 - (3) increasing bp – bp repulsion
 - (4) increasing p-orbital character in sp^3
- In which of the following ionization process, the bond order has increased and the magnetic behaviour has changed [AIEEE-2007]
 - (1) $\text{NO} \rightarrow \text{NO}^+$
 - (2) $\text{O}_2 \rightarrow \text{O}_2^+$
 - (3) $\text{N}_2 \rightarrow \text{N}_2^+$
 - (4) $\text{C}_2 \rightarrow \text{C}_2^+$
- Which of the following species exhibits the diamagnetic behaviour [AIEEE-2007]
 - (1) O_2^+
 - (2) O_2
 - (3) NO
 - (4) O_2^{2-}
- which one of the following pairs of species have the same bond order? [AIEEE-2008]
 - (1) CN^- and NO^+
 - (2) CN^- and CN^+
 - (3) O_2^- and CN^-
 - (4) NO^+ and CN^+

12. The bond dissociation energy of B–F in BF_3 is 646 kJ mol^{-1} whereas that of C–F in CF_4 is 515 kJ mol^{-1} . The correct reason for higher B–F bond dissociation energy as compared to that of C–F is :- [AIEEE-2009]
- Significant $p\pi - p\pi$ interaction between B and F in BF_3 whereas there is not possibility of such interaction between C and F in CF_4 .
 - Lower degree of $p\pi - p\pi$ interaction between B and F in BF_3 than that between C and F in CF_4
 - Smaller size of B-atom as compared to that of C-atom
 - Stronger σ bond between B and F in BF_3 as compared to that between C and F in CF_4
13. Using MO theory predict which of the following species has the shortest bond length ? [AIEEE-2009]
- O_2^-
 - O_2^{2-}
 - O_2^{2+}
 - O_2^+
14. Among the following the maximum covalent character is shown by the compound :- [AIEEE-2011]
- AlCl_3
 - MgCl_2
 - FeCl_2
 - SnCl_2
15. Which one of the following molecules is expected to exhibit diamagnetic behaviour ?
- C_2
 - N_2
 - O_2
 - S_2 [AIEEE-2013]
16. In which of the following pairs of molecules/ions, both the species are not likely to exist ?
- $\text{H}_2^+, \text{He}_2^{2-}$
 - $\text{H}_2^-, \text{He}_2^{2-}$
 - $\text{H}_2^{2+}, \text{He}_2$
 - $\text{H}_2^-, \text{He}_2^{2+}$ [JEE-M-2013]
17. Stability of the species Li_2 , Li_2^- and Li_2^+ increases in the order of :- [JEE-M-2013]
- $\text{Li}_2 < \text{Li}_2^+ < \text{Li}_2^-$
 - $\text{Li}_2^- < \text{Li}_2^+ < \text{Li}_2$
 - $\text{Li}_2 < \text{Li}_2^- < \text{Li}_2^+$
 - $\text{Li}_2^- < \text{Li}_2 < \text{Li}_2^+$
18. Which one of the following properties is **not** shown by NO ? [JEE-M-2014]
- It combines with oxygen to form nitrogen dioxide
 - It's bond order is 2.5
 - It is diamagnetic in gaseous state
 - It is a neutral oxide
19. The correct order of thermal stability of hydroxides is : [JEE-M-2015 (on line)]
- $\text{Ba(OH)}_2 < \text{Sr(OH)}_2 < \text{Ca(OH)}_2 < \text{Mg(OH)}_2$
 - $\text{Mg(OH)}_2 < \text{Sr(OH)}_2 < \text{Ca(OH)}_2 < \text{Ba(OH)}_2$
 - $\text{Mg(OH)}_2 < \text{Ca(OH)}_2 < \text{Sr(OH)}_2 < \text{Ba(OH)}_2$
 - $\text{Ba(OH)}_2 < \text{Ca(OH)}_2 < \text{Sr(OH)}_2 < \text{Mg(OH)}_2$
20. Which of the alkaline earth metal halides given below is essentially covalent in nature :- [JEE-M-2015 (on line)]
- SrCl_2
 - CaCl_2
 - BeCl_2
 - MgCl_2
21. Which one of the following alkaline earth metal sulphates has its hydration enthalpy greater than its lattice enthalpy ? [JEE-M-2015]
- BaSO_4
 - SrSO_4
 - CaSO_4
 - BeSO_4

22. The intermolecular interaction that is dependent on the inverse cube of distance between the molecules is :- [JEE-M-2015]
 (1) London force (2) Hydrogen bond
 (3) ion-ion interaction (4) ion-dipole interaction
23. Which one has the highest boiling point ? [JEE-M-2015]
 (1) Kr (2) Xe (3) He (4) Ne
24. Which intermolecular force is most responsible in allowing xenon gas to liquefy? [JEE (MAIN) ONLINE 2016]
 (1) Ionic
 (2) Instantaneous dipole- induced dipole
 (3) Dipole - dipole
 (4) Ion - dipole
25. The bond angle H-X-H is the greatest in the compound : [JEE (MAIN) ONLINE 2016]
 (1) NH_3 (2) H_2O (3) PH_3 (4) CH_4
26. Which of the following species is not paramagnetic :- [JEE-MAINS-2017]
 (1) NO (2) CO (3) O_2 (4) B_2
27. Which of the following is paramagnetic ? [JEE-MAINS-2017 (On-line)]
 (1) CO (2) O_2^{2-} (3) NO^+ (4) B_2
28. sp^3d^2 hybridization is not displayed by : [JEE-MAINS-2017 (On-line)]
 (1) $[\text{CrF}_6]^{3-}$ (2) BrF_5 (3) PF_5 (4) SF_6
29. The number of S=O and S-OH bonds present in peroxodisulphuric acid and pyrosulphuric acid respectively are : [JEE-MAINS-2017 (On-line)]
 (1) (2 and 4) and (2 and 4) (2) (4 and 2) and (2 and 4)
 (3) (2 and 2) and (2 and 2) (4) (4 and 2) and (4 and 2)
30. The correct sequence of decreasing number of π -bonds in the structures of H_2SO_3 , H_2SO_4 and $\text{H}_2\text{S}_2\text{O}_7$ is:- [JEE-MAINS-2017 (On-line)]
 (1) $\text{H}_2\text{S}_2\text{O}_7 > \text{H}_2\text{SO}_4 > \text{H}_2\text{SO}_3$ (2) $\text{H}_2\text{SO}_3 > \text{H}_2\text{SO}_4 > \text{H}_2\text{S}_2\text{O}_7$
 (3) $\text{H}_2\text{S}_2\text{O}_7 > \text{H}_2\text{SO}_3 > \text{H}_2\text{SO}_4$ (4) $\text{H}_2\text{SO}_4 > \text{H}_2\text{S}_2\text{O}_7 > \text{H}_2\text{SO}_3$
31. The increasing order of the boiling points for the following compounds is:- [JEE-MAINS-2017 (On-line)]
 (I) $\text{C}_2\text{H}_5\text{OH}$ (II) $\text{C}_2\text{H}_5\text{Cl}$ (III) $\text{C}_2\text{H}_5\text{CH}_3$ (IV) $\text{C}_2\text{H}_5\text{OCH}_3$
 (1) (III) < (II) < (I) < (IV) (2) (II) < (III) < (IV) < (I)
 (3) (IV) < (III) < (I) < (II) (4) (III) < (IV) < (II) < (I)
32. The number of P-OH bonds and the oxidation state of phosphorus atom in pyrophosphoric acid ($\text{H}_4\text{P}_2\text{O}_7$) respectively are :- [JEE-MAINS-2017 (On-line)]
 (1) five and four (2) five and five (3) four and five (4) four and four
33. The group having triangular planar structures is :- [JEE-MAINS-2017 (On-line)]
 (1) CO_3^{2-} , NO_3^- , SO_3 (2) NCl_3 , BCl_3 , SO_3 (3) NH_3 , SO_3 , CO_3^{2-} (4) BF_3 , NF_3 , CO_3^{2-}

34. Which of the following are Lewis acids ? [JEE-MAINS-2018]

- (1) AlCl_3 and SiCl_4 (2) PH_3 and SiCl_4 (3) BCl_3 and AlCl_3 (4) PH_3 and BCl_3

35. According to molecular orbital theory, which of the following will not be a viable molecule ?

[JEE-MAINS-2018]

- (1) He_2^+ (2) H_2^- (3) H_2^{2-} (4) He_2^{2+}

36. Which of the following compounds contain(s) no covalent bond(s) ?

[JEE-MAINS-2018]

KCl , PH_3 , O_2 , B_2H_6 , H_2SO_4

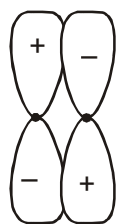
- (1) KCl , H_2SO_4 (2) KCl (3) KCl , B_2H_6 (4) KCl , B_2H_6 , PH_3

37. In KO_2 , the nature of oxygen species and the oxidation state of oxygen atom are, respectively

[JEE-MAINS-2018 (Online)]

- (1) Superoxide and $-1/2$ (2) Oxide and -2
(3) Peroxide and $-1/2$ (4) Superoxide and -1

38. Which of the following best describes the diagram below of a molecular orbital ?



[JEE-MAINS-2018 (Online)]

- (1) An antibonding π orbital (2) An antibonding σ orbital
(3) A non-bonding orbital (4) A bonding π orbital

39. In the molecular orbital diagram for the molecular ion, N_2^+ , the number of electrons in the σ_{2p} molecular orbital is :-

[JEE-MAINS-2018 (Online)]

- (1) 3 (2) 1 (3) 0 (4) 2

40. Xenon hexafluoride on partial hydrolysis produces compounds 'X' and 'Y'. Compounds 'X' and 'Y' and the oxidation state of Xe are respectively :

[JEE-MAINS-2018 (Online)]

- (1) $\text{XeO}_2\text{F}_2(+6)$ and $\text{XeO}_2(+4)$ (2) $\text{XeOF}_4(+6)$ and $\text{XeO}_2\text{F}_2(+6)$
(3) $\text{XeOF}_4(+6)$ and $\text{XeO}_3(+6)$ (4) $\text{XeO}_2(+4)$ and $\text{XeO}_3(+6)$

41. Which of the following is a Lewis acid ?

[JEE-MAINS-2018 (Online)]

- (1) NaH (2) NF_3 (3) PH_3 (4) $\text{B}(\text{CH}_3)_3$

42. A group 13 element 'X' reacts with chlorine gas to produce a compound XCl_3 . XCl_3 is electron deficient and easily reacts with NH_3 to form $\text{Cl}_3\text{X} \leftarrow \text{NH}_3$ adduct; however, XCl_3 does not dimerize. X is :-

[JEE-MAINS-2018 (Online)]

- (1) Ga (2) Al (3) In (4) B

43. Which of the following conversions involves change in both shape and hybridisation ?

[JEE-MAINS-2018 (Online)]

- (1) $\text{BF}_3 \rightarrow \text{BF}_4^-$ (2) $\text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+$ (3) $\text{CH}_4 \rightarrow \text{C}_2\text{H}_6$ (4) $\text{NH}_3 \rightarrow \text{NH}_4^+$

13. Match each of the diatomic molecules/ions in Column I with its property / properties in Column II. [JEE 2009]

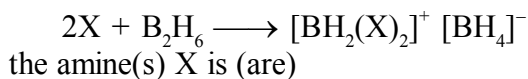
Column I

- (A) B_2
(B) N_2
(C) O_2^-
(D) O_2

Column II

- (P) Paramagnetic
(Q) undergoes oxidation
(R) Undergoes reduction
(S) Bond order ≥ 2
(T) Mixing of 's' and 'p' orbitals

14. In the reaction



- (A) NH_3 (B) CH_3NH_2 (C) $(CH_3)_2NH$ (D) $(CH_3)_3N$

15. The species having pyramidal shape is

- (A) SO_3 (B) BrF_3 (C) SiO_3^{2-} (D) OSF_2

16. Assuming that Hund's rule is violated, the bond order and magnetic nature of the diatomic molecule B_2 is [JEE 2010]

- (A) 1 and diamagnetic (B) 0 and diamagnetic (C) 1 and paramagnetic (D) 0 and paramagnetic

Subjective

17. The value of n in the molecular formula $Be_nAl_2Si_6O_{18}$ is [JEE 2010]

18. The total number of diprotic acids among the following is [JEE 2010]

- H_3PO_4 H_2SO_4 H_3PO_3 H_2CO_3 $H_2S_2O_7$
 H_3BO_3 H_3PO_2 H_2CrO_4 H_2SO_3



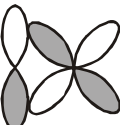
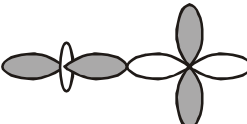
19. Among the following, the number of elements showing only one non-zero oxidation state is [JEE 2010]
O, Cl, F, N, P, Sn, Tl, Na, Ti

20. Assuming 2s-2p mixing is NOT operative, the paramagnetic species among the following is : [JEE Adv. 2014]

- (A) Be_2 (B) B_2 (C) C_2 (D) N_2

21. Match the orbital overlap figures shown in List-I with the description given in List-II and select the correct answer using the code given below the lists. [JEE Adv. 2014]

List-I

- (P) 
(Q) 
(R) 
(S) 

List-II

- (1) p - d π antibonding
(2) d - d σ bonding
(3) p - d π bonding
(4) d - d σ antibonding

Code :

- | | P | Q | R | S |
|-----|---|---|---|---|
| (A) | 2 | 1 | 3 | 4 |
| (C) | 2 | 3 | 1 | 4 |

- | | P | Q | R | S |
|-----|---|---|---|---|
| (B) | 4 | 3 | 1 | 2 |
| (D) | 4 | 1 | 3 | 2 |

22. Three moles of B_2H_6 are completely reacted with methanol. The number of moles of boron containing product formed is - [JEE Adv. 2015]
23. When O_2 is adsorbed on a metallic surface, electron transfer occurs from the metal to O_2 . The TRUE, statement (s) regarding this adsorption is (are) [JEE Adv. 2015]
 (A) O_2 is physisorbed (B) heat is released
 (C) occupancy of π_{2p}^* of O_2 is increased (D) bond length of O_2 is increased
24. According to Molecular Orbital Theory, [JEE Adv. 2016]
 (A) C_2^{2-} is expected to be diamagnetic
 (B) O_2^{2+} is expected to have a longer bond length than O_2
 (C) N_2^+ and N_2^- have the same bond order
 (D) He_2^+ has the same energy as two isolated He atoms
25. The colour of the X_2 molecules of group 17 elements changes gradually from yellow to violet down the group. This is due to - [JEE Adv. 2017]
 (A) the physical state of X_2 at room temperature changes from gas to solid down the group
 (B) decrease in HOMO-LUMO gap down the group
 (C) decrease in $\pi^*-\sigma^*$ down the group
 (D) decrease in ionization energy down the group
26. Among H_2 , He_2^+ , Li_2 , Be_2 , B_2 , C_2 , N_2 , O_2^- , and F_2 , the number of diamagnetic species is - (Atomic number) : H = 1, He = 2, Li = 3, Be = 4, B = 5, C = 6, N = 7, O = 8, f = 9) [JEE Adv. 2017]
27. The sum of the number of lone pairs of electrons on each central atom in the following species is. [JEE Adv. 2017]
 $[TeBr_6]^{2-}$, $[BrF_2]^+$, SNF_3 and $[XeF_3]^-$
 [Atomic number : N = 7, F = 9, S = 16, Br = 35, Te = 52, Xe = 54]
28. The option(s) with only amphoteric oxides is (are): [JEE Adv. 2017]
 (A) Cr_2O_3 , CrO , SnO , PbO (B) NO , B_2O_3 , PbO , SnO_2
 (C) Cr_2O_3 , BeO , SnO , SnO_2 (D) ZnO , Al_2O_3 , PbO , PbO_2
29. Among the following, the correct statement(s) is are [JEE Adv. 2017]
 (A) $Al(CH_3)_3$ has the three-centre two-electron bonds in its dimeric structure
 (B) $AlCl_3$ has the three-centre two-electron bonds in its dimeric structure
 (C) BH_3 has the three-centre two-electron bonds in its dimeric structure
 (D) The Lewis acidity of BCl_3 is greater than that of $AlCl_3$
30. Based on the compounds of group 15 elements, the correct statement(s) is (are) [JEE Adv. 2018]
 (A) Bi_2O_5 is more basic than N_2O_5
 (B) NF_3 is more covalent than BiF_3
 (C) PH_3 boils at lower temperature than NH_3
 (D) The N-N single bond is stronger than the P-P single bond

ANSWERS KEY

EXERCISE # O-1

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	A	D	D	B	A	C	C	B	A	C
Que.	11	12	13	14	15	16	17	18	19	20
Ans.	C	A	C	B	B	B	A	D	D	A
Que.	21	22	23	24	25	26	27	28	29	30
Ans.	B	C	C	D	D	D	C	A	A	D
Que.	31	32	33	34	35	36	37	38	39	40
Ans.	A	B	D	B	A	A	A	B	D	C
Que.	41	42	43	44	45	46	47	48	49	50
Ans.	C	A	C	C	B	A	D	A	A	B

EXERCISE # O-2

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	A, B, C	A, B, C	A, B, C	A, B, D	A, B	A, C	A, B, C	B, C	A, C	A, B, C
Que.	11	12	13	14	15	16	17	18	19	20
Ans.	B, C, D	B, C, D	B, C	B, C, D	C, D	A, B, C	A, C, D	A, C	A, C	A, D
Que.	21	22	23	24	25	26	27	28	29	30
Ans.	A, B, D	B, C, D	A, B, C	A, B, C	A, B, D	B, D	A, B, C, D	A, B	A, B, C	A, B, D
Que.	31	32								
Ans.	A, B, C	B, C, D								

EXERCISE # S-1

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	3	8	4	2	2	105	4	3	2	4

EXERCISE # S-2

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	D	A	B	A	D	A	B	B	B	D
Que.	11	12	13	14				15		
Ans.	C	B	C	(A)-Q,R,S (B)-P,Q,S (C)-S (D)-P,Q				(A)-P,S (B)-Q,T (C)-R (D)-P,S		
Que.	16					17	18	19		
Ans.	(A)-P,R,T (B)-Q (C)-Q (D)-Q,T					B	C	D		

EXERCISE # J-MAINS

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	2	3	4	2	3	4	1	4	1	4
Que.	11	12	13	14	15	16	17	18	19	20
Ans.	1	1	3	1	2	3	2	3	3	3
Que.	21	22	23	24	25	26	27	28	29	30
Ans.	4	2	2	2	4	2	4	1 & 3	4	1
Que.	31	32	33	34	35	36	37	38	39	40
Ans.	4	3	1	3	3	2	1	1	2	2
Que.	41	42	43							
Ans.	4	4	1							

EXERCISE # J-ADVANCE

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	B, C	A, C	A	B	B	A	C	B	D	A
Que.	11	12	13					14	15	16
Ans.	C	C	(A)-P, Q, R, T (B)-Q, R, S, T (C)-P, Q, R (D)-P, Q, R, S					B, C	D	A
Que.	17	18	19	20	21	22	23	24	25	26
Ans.	3	6	2	C	C	6	B, C, D	A, C	B, C	5 or 6
Que.	27	28	29	30						
Ans.	6	C, D	A, C, D	A, B, C						

CO-ORDINATION CHEMISTRY

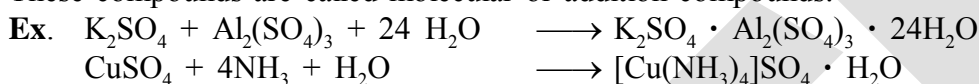
□ INTRODUCTION :

- The concept of co-ordination compounds arises from the complex formation tendency of transition elements.
- These compounds play a vital role in our lives, as chlorophyll of plants, vitamin B₁₂ and haemoglobin of animal blood are the co-ordination compounds of Mg, Co and Fe respectively.
- The co-ordination compounds play important role in analytical chemistry, polymerisation reactions, metallurgy and refining of metals, photography, water purification etc.
- Co-ordination compounds also find many applications in electroplating, textile dyeing and medicinal chemistry.

□ ADDITION COMPOUNDS :

When solutions containing two or more salts in simple molecular proportion are evaporated, crystals of new compound separate out.

These compounds are called molecular or addition compounds.



These addition compounds can be divided into two classes :

(A) DOUBLE SALTS :

Those which lose their identity in solution

In solutions these compounds break down into simpler ions. Such addition compounds which lose their identity in solutions are called **double salts**.

Example :

Potash alum $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ when dissolved in water breaks down into K^+ , SO_4^{2-} , Al^{+3} ions and therefore is an example of **double salt**.

(B) COORDINATION COMPOUNDS :

Those which retain their identity in solution.

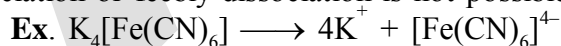
In aqueous solution, these addition compounds do not furnish all simple ions but instead give more complex ions having complicated structure.

Example :

Potassium ferrocyanide $\text{K}_4[\text{Fe}(\text{CN})_6]$ does not furnish simple K^+ , Fe^{2+} and CN^- ions but gives K^+ ions and complex ferrocyanide ions, $[\text{Fe}(\text{CN})_6]^{4-}$. These types of compounds are called **complex compounds or co-ordination compounds**.

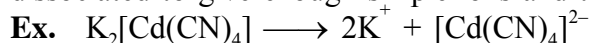
On the basis of stability of complex ion, complex ions are further divided as follows –

- Perfect complexes :** The compounds in which complex ion is fairly stable and further dissociation or feeble dissociation is not possible in solution state.



The ferrocyanide ion $[\text{Fe}(\text{CN})_6]^{4-}$ is so insignificantly dissociated that it can be considered as practically undissociated and does not give the qualitative test of Fe^{2+} or CN^- ions..

- Imperfect complexes :** Those complexes in which complex ion is less stable and is reversibly dissociated to give enough simple ions and thus respond to their usual qualitative test.



□ DEFINITIONS OF TERMS USED IN CO-ORDINATION COMPOUNDS

- (a) **Co-ordination or complex compound :** Co-ordination compounds are those molecular compounds which retain their identity even when dissolved in water or any other solvent and their properties are completely different from those of the constituent ions.
- (b) **Central ion :** The cation to which one or more neutral molecules or ions are attached is called the atom / ion. Since, the central ion acts as an acceptor and thus has to accommodate electron pairs donated by the donor atoms of neutral molecules or ions, it must have empty orbitals of appropriate energy.
- (c) **Complex ion :** A complex ion may be defined as an electrically charged radical which is formed by the combination of a simple cation with one/more neutral molecules or one/more simple.
- (d) **Co-ordination number :** The total number of co-ordinate covalent bond formed by central metal in complex is called the co-ordination number of the central metal ion .

Some common co-ordination number of important metals are as given below.

Metal	Coordination Number	Metal	Coordination Number
Cu^+	2, 4	Ni^{2+}	4, 6
Ag^+	2	Fe^{2+}	4, 6
Au^+	2, 4	Fe^{3+}	6
Hg_2^{2+}	2	Co^{2+}	4, 6
Cu^{2+}	4, 6	Co^{3+}	6
Ag^{2+}	4	Al^{3+}	6
Pt^{2+}	4	Sc^{3+}	6
Pd^{2+}	4	Pt^{4+}	6
Mg^{2+}	6	Pd^{4+}	6

Example. Coordination number of the central metal ions in

- (i) $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is four (ii) $[\text{Fe}(\text{EDTA})]^-$ is six

- (e) **Co-ordination sphere :** The part of the complex enclosed in square bracket is known as co-ordination sphere. It is actually combination of central metal and ligands.
- (f) **Ligands :**
- (a) The ions or neutral molecules which combine with central metal ion to form complex are called ligands.
- (b) They act as electron pair donor (i.e. Lewis bases) though certain ligands also accept electron from central metal and such ligands are known as π - acid ligands.

❖ CLASSIFICATION OF LIGANDS

(A) Based on charge

(i) Neutral ligands : H_2O , NO , CO , C_6H_6 etc.

(ii) Positive ligands : NO^+ , N_2H_5^+

(iii) Negative ligands : Cl^- , NO_2^- , CN^- , OH^-

(B) Based on denticity

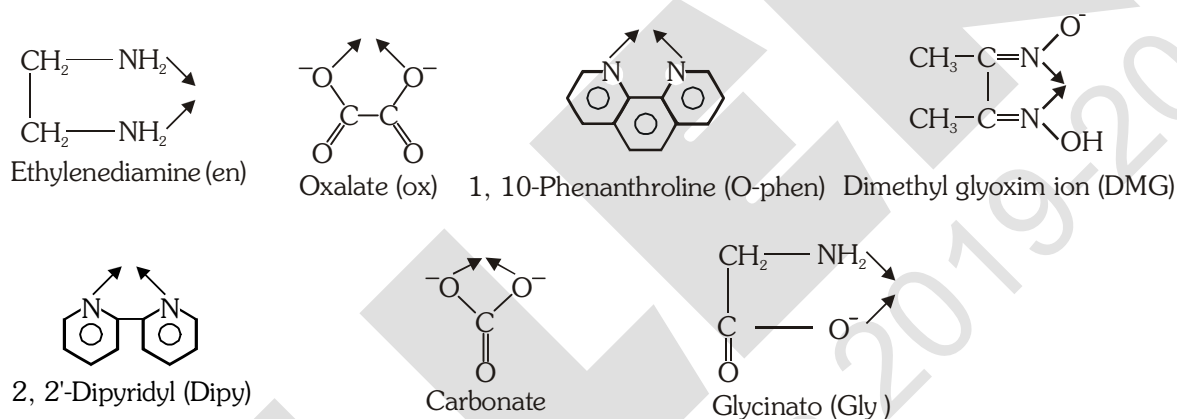
The number of electron pairs donated to central metal by a particular ligand is known as DENTICITY. Depending on number of electron pairs donated, these are classified in following categories.

(a) Unidentate/monodentate ligands

Ligands which donate one pair of electron to the central metal are called unidentate ligands. X^- , CN^- , NO_2^- , NH_3 , Pyridine, OH^- , NO_3^- , H_2O , SO_3^{2-} , CO , NO , OH^- , O^{2-} , $(\text{C}_6\text{H}_5)_3\text{P}$ etc.

(b) Bidentate ligands

Ligands which have two donor atoms and have the ability to link with central metal ion at two positions are called bidentate ligands.



(c) Tridentate ligands

The ligands which donate three pairs of electrons to the central metal are called tridentate ligands

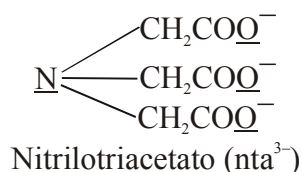
Example.



(d) Tetradentate ligands

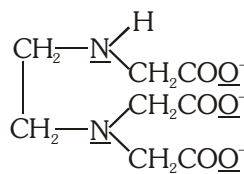
Those ligands which can donate four electron pairs to the central metal are known as tetradentate ligands,

Example : (Underline atoms are donating atom)



- (e) **Pentadentate ligands** : Those ligands which can give five electron pairs to the central metal are known as pentadentate ligands.

Example : Ethylenediaminetriacetate ion. (Underline atoms are donating atom)

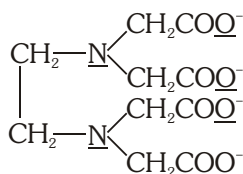


(EDTA)⁻³

Ethylenediaminetriacetate ion

- (f) **Hexadentate ligands** : Those ligands which can donate six electron pairs to the central metal are known as hexadentate ligands.

Example : (Underline atoms are donating atom)

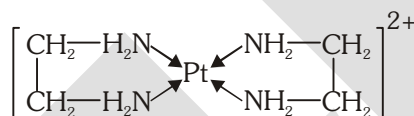


Ethylenediaminetetraacetate ion (EDTA)⁻⁴

- (g) **Chelating ligands**

Polydentate ligands whose structures permit the attachment of two or more donor sites to metal ion simultaneously, thus resulting in cyclic structure are called chelating ligands and compound formed is known as **chelate compound**.

Example :



- (h) **Ambidentate ligands**

Ligands which can ligate through two different atoms present in it are called ambidentate ligands. At a time only one atom can donate.



Example :

CN⁻ can coordinate through either the nitrogen or the carbon atom to central metal ion.

- (i) **Flexidentate ligands**

Ligands which sometimes do not use all the donor sites to get coordinated with central metal ion are known as flexidentate ligands.

Ex. SO₄²⁻, CO₃²⁻ etc.

- (C) Based upon bonding interaction between the ligand and the central atom.

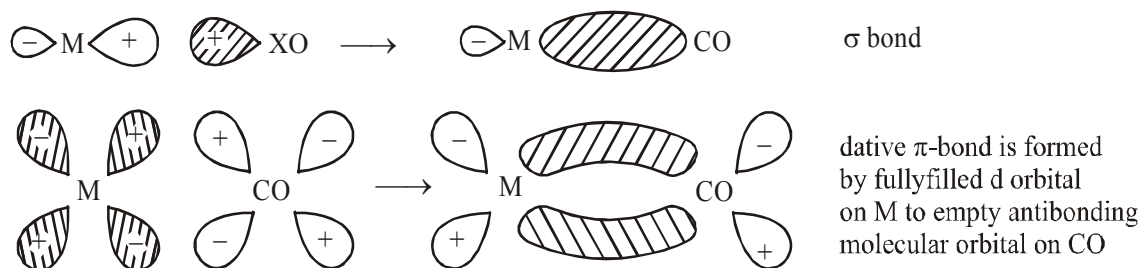
- (i) **Classical or simple ligand** : These ligand only donate the lone pair of electrons to the central atom.

eg. : O²⁻, OH⁻, F⁻ etc.

- (ii) **Non classical or π-acid or π-acceptor ligand** : These ligand not only donate the lone pair of electrons to central metal but also accept the electron cloud from central atom

eg. : CO, CN⁻, NO⁺, PF₃, PR₃ etc.

BONDING IN METAL CARBONYL : Ex. $[\text{Fe}(\text{CO})_5]$; $[\text{Ni}(\text{CO})_4]$; $[\text{Cr}(\text{CO})_6]$



Schematic diagram of orbital overlaps in metal carbonyls.

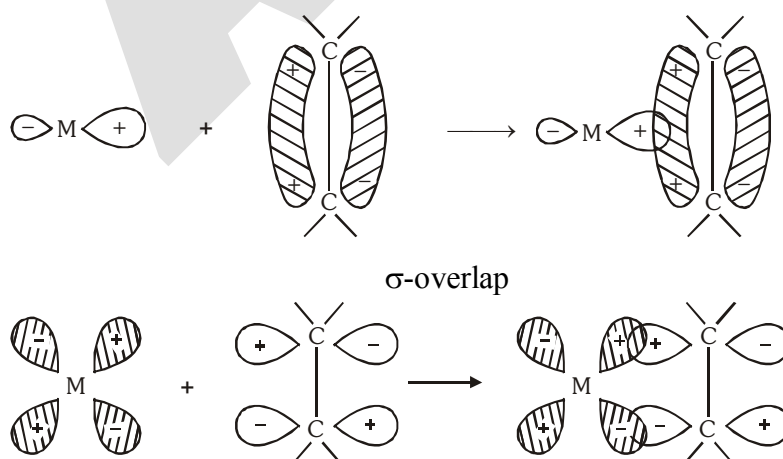
- The metal-carbon bond in metal carbonyls may be represented as the donation of an electron pair from carbon to vacant orbital of metal & form σ bond ($\text{M} \leftarrow \text{CO}$).
- A second bond is formed by back bonding sometimes called dative π -bonding. This arises from side ways overlap of a full orbital on the metal with the empty antibonding π^*p_y/π^*p_z (if x-axis is molecular axis) molecular orbital of the carbon monoxide, thus forming a $\pi \text{ M} \xrightarrow{d\pi-p\pi} \text{CO}$ bond ($d\pi-p\pi$ back bond).
- The filling or partial filling, of the antibonding orbital on CO reduces the bond order of C–O bond from the triple bond in CO towards a double bond. This shown by the increase in C–O bond length from 1.128 Å in CO to about 1.15 Å in many carbonyls.
- Since CO accept the back donated electrons from the metal atom in to its vacant π^* orbital, CO is called π -acid or π -acceptor ligand or π -bonding ligand. Other such π -acid ligands are— CN^- , RCN , NO^+ .

Note:- π -acid ligands like PF_3 , PPh_3 , AsCl_3 etc. accept the back donated electrons from the metal atom in to its vacant d-orbital of central atom.

Bonding in π -bonded organo metallic compound. Like zeises salt $\text{K} [\text{PtCl}_3(\pi\text{-C}_2\text{H}_4)]$

The bonding of alkenes to a transition metal to form complexes has two components. First, the π -electron density of the alkene overlaps with a σ -type vacant orbital or the metal atom.

Second is the π back bond formed by the flow of electron density from a filled d-orbital on the metal into the vacant π^* -antibonding molecular orbital on the alkene molecule as shown below :



□ IUPAC NOMENCLATURE OF COORDINATION COMPOUNDS

The main rules of naming of complexes are –

- (a) Like simple salts, the positive part of the coordination compound is named first.

Ex. $K_4[Fe(CN)_6]$ the naming of this complex starts with potassium.

$[Cr(NH_3)_6]Cl_3$ the naming of this complex starts with name of complex ion.

- (b) Naming of coordination sphere :- The names of ligands along with their numerical prefixes (to represent their no) are written first, followed by the name of central metal.

- (c) The ligands can be neutral, anionic or cationic.

- (i) The neutral ligands are named as the molecule **Ex.** C_5H_5N pyridine, $(C_6H_5)_3P$ Triphenyl phosphine.

$H_2N-CH_2-CH_2-NH_2$ ethylene diamine.

The neutral ligands which are not named as the molecule are CO carbonyl, NO nitrosyl, H_2O Aqua, NH_3 ammine.

- (ii) Anionic ligands ending with 'ide' are named by replacing the 'ide' with suffix 'O'.

Symbol	Name as ligand	Symbol	Name as ligand
Cl^-	Chloro/Chlorido	N^{3-}	Nitrido
Br^-	Bromo/Bromido	O_2^{2-}	Peroxo/Peroxido
CN^-	Cyano/Cyanido	O_2H^-	Perhydroxo/Perhydroxido
O^{2-}	Oxo/Oxido	S^{2-}	Sulphido
OH^-	Hydroxo/Hydroxido	NH^{2-}	Imido
H^-	Hydrido/Hydrido	NH_2^-	Amido

Ligands whose names end in 'ite' or 'ate' become 'ito' i.e., by replacing the ending 'e' with 'o' as follows.

Symbol	Name as ligand	Symbol	Name as ligand
CO_3^{2-}	Carbonato	SO_3^{2-}	Sulphito
$C_2O_4^{2-}$	Oxalato	CH_3COO^-	Acetato
SO_4^{2-}	Sulphato	ONO^-	(bonded through oxygen) nitrito
NO_3^-	Nitrato	NO_2^-	(bonded through nitrogen) nitro
$S_2O_3^{2-}$	Thiosulphato		

- (iii) Positive ligands naming ends in 'ium' $NH_2-NH_3^+$ Hydrazinium, NO^+ nitrosonium/nitrosylium.

- (d) If ligands are present more than once, then their number is indicated by prefixes like di, tri, tetra etc.
- (e) If words like di, tri, tetra are already used in the naming of ligand, or if it is polydentate ligand or organic ligand, the prefixes bis-, tris-, tetrakis-, pentakis- etc. are used to specify their number.

Example : $[Pt(en)_2Cl_2]Cl_2$: Dichlorobis(ethylenediamine)platinum(IV) chloride.

- (f) When more than one type of ligands are present in the complex, then the ligands are named in the alphabetical order.
- (g) After naming of ligands the central metal ion is to be named followed by its oxidation state in Roman numbers in brackets. (as per IUPAC)

If the complex is neutral or provides a cationic complex ion, then the central metal ion is to be named as it is.

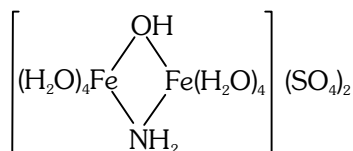
If the complex provides anionic complex ion then the name of central metal ion ends with 'ate'

Example : $(\text{NH}_4)_2[\text{CuCl}_4]$: Ammonium tetrachloridocuprate(II)

- (h) After the naming of central metal ion, anion which is in the outer sphere is to be named. The naming of some of the complexes is done as follows – (as per IUPAC)

Complex Compounds		IUPAC Name
(i)	$\text{K}_4[\text{Fe}(\text{CN})_6]$ (anionic complex) so suffix 'ate' is added with metal name	Potassium hexacyanoferrate(II)
(ii)	$\text{K}_2[\text{Pt Cl}_6]$	Potassium hexachloridoplatinate(IV)
(iii)	$[\text{Co}(\text{NH}_3)_6] \text{Cl}_3$ (Cationic complex) so metal is without any suffix	Hexamminecobalt(III) chloride
(iv)	$[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2] \text{Cl}$	Tetraaquadichloridochromium(III) chloride
(v)	$[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$	Diamminetetrachloridoplatinum(IV)
(vi)	$[\text{Co}(\text{NH}_3)_3 \text{Cl}_3]$ (Neutral complex) So no suffix is used with metal ion	Triamminetrichloridocobalt(III)
(vii)	$\text{K}_3[\text{Co}(\text{NO}_2)_6]$	Potassium hexanitrocobaltate(III)
(viii)	$\text{Na}_3[\text{Fe}(\text{CN})_5 \text{NO}]$	Sodium pentacyanonitrosylferrate(II)
(ix)	$[\text{NiCl}_4]^{-2}$	Tetrachloridonickelate(II) ion
(x)	$[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{+2}$	Pentamminechloridoruthenium(III) ion
(xi)	$[\text{Fe}(\text{en})_3]\text{Cl}_3$	Tris(ethylenediamine)iron(III) chloride
(xii)	$[\text{Ni}(\text{Gly})_2]$	Bis(glycinato)nickel(II)

- (i) If a complex ion has two metal atoms then it is termed polynuclear. The ligand which connects the two metal ions is called as **Bridging ligand or Bridge group**.
A prefix of Greek letter μ , is repeated before the name of each different kind of bridging group.



Tetraaquaairon(III)- μ -amido- μ -hydroxotetraaquaairon(III) sulphate

FORMATION OF CO-ORDINATION COMPOUNDS

It can be explained by number of theories.

- (A) Werner's co-ordination theory
- (B) Sidwick theory or Effective Atomic Number Theory (EAN)
- (C) Valence bond theory
- (D) Crystal field theory

(A) WERNER'S CO-ORDINATION THEORY :

Werner's co-ordination theory was the first attempt to explain the bonding in co-ordination compounds. The main postulates of this theory are :

- (a) Metals possesses two types of valencies - Primary valency and secondary valency.
- (b) Primary valencies are normally ionisable and are exhibited by a metal in the formation of its simple salts such as CoCl_3 , CuSO_4 and AgCl . In these salts the primary valencies of Co, Cu and Ag are 3, 2, 1 respectively. Primary valencies are referred to as oxidation state of their metal ion.
- (c) Secondary valencies are non-ionisable and are exhibited by a metal in the formation of its complex ions such as $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Cu}(\text{NH}_3)_4]^{2+}$ and $[\text{Ag}(\text{NH}_3)_2]^+$. In these complex, the secondary valencies of Co^{3+} , Cu^{2+} , Ag^+ are 6, 4 and 2 respectively. These are referred to as co-ordination number (C.N.) of the metal cation.
- (d) Primary linkages (valencies) are satisfied by negative ions while secondary valencies are satisfied by neutral molecules, negative ions or in some cases positive ions also.
- (e) Every metal atom or ion has a fixed number of secondary valencies. In other words, the co-ordination number of the metal atom is usually fixed.
- (f) Every metal has tendency to satisfy both its primary and secondary valencies.
- (g) The ligands satisfying secondary valency are always directed towards fixed positions in space about the central metal atom or ion. Thus, the co-ordination compounds have a definite geometry. Werner deduced that in $\text{CoCl}_3 \cdot 5\text{NH}_3$ only two of the three chlorine atoms are ionic and 5 NH_3 and one Cl form co-ordinate bonds to Co^{3+} ion.

Formula of some cobalt complexes.

Example :

Old	New	No. of Cl^- ions precipitated	Total No. of ions
(i) $\text{CoCl}_3 \cdot 6 \text{NH}_3$	$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$	3	4
(ii) $\text{CoCl}_3 \cdot 5 \text{NH}_3$	$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	2	3
(iii) $\text{CoCl}_3 \cdot 4 \text{NH}_3$	$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$	1	2

Complex	Modern formula	No. of Cl^- ions precipitated	Total number of ions
$\text{PtCl}_4 \cdot 6\text{NH}_3$	$[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$	4	5
$\text{PtCl}_4 \cdot 5\text{NH}_3$	$[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Cl}_3$	3	4
$\text{PtCl}_4 \cdot 4\text{NH}_3$	$[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2$	2	3
$\text{PtCl}_4 \cdot 3\text{NH}_3$	$[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]\text{Cl}$	1	2
$\text{PtCl}_4 \cdot 2\text{NH}_3$	$[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$	0	0 (non-electrolyte)

❖ WERNER'S REPRESENTATION OF COMPLEXES

(i)	$\text{Fe}(\text{NH}_3)_6\text{Cl}_3$		$[\text{Fe}(\text{NH}_3)_6]\text{Cl}_3$ Dotted lines indicate primary valency and continuous lines indicate secondary valency of metal ion.
(ii)	$\text{Fe}(\text{NH}_3)_5\text{Cl}_3$		$[\text{Fe}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ In this complex two 'Cl' groups act as primary valencies and one of the 'Cl' acts as secondary valency also.
(iii)	$\text{Fe}(\text{NH}_3)_4\text{Cl}_3$		$[\text{Fe}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ In this complex one 'Cl' group act as primary valency and two of the 'Cl' groups act as secondary valencies also.

(B) SIDWICK THEORY OR EFFECTIVE ATOMIC NUMBER CONCEPT (EAN)

Sidwick proposed effective atomic number theory to explain the stability of the complexes. Total number of electrons on central metal including those transferred from ligands is known as EAN. The EAN generally coincides with the atomic number of next inert gas except in some cases.

EAN can be calculated by the following relation :

EAN = (atomic number of the metal – oxidation state of central metal with sign) + number of electrons gained from the donor atoms of the ligands.

Example Effective atomic number of the metal atom in the following :

- (a) $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$ is 33 (b) $\text{K}_4[\text{Fe}(\text{CN})_6]$ is 36

(C) VALENCE BOND THEORY

The main features of this theory are -

- Every metal ion when it forms a complex compound undergoes formation of coordinate covalent bond.
- During this bond formation, the metal ion acts as electron pair acceptor. For this the metal ion provides vacant orbitals.
- The number of vacant orbitals provided is equal to the coordination number of metal ion.

Example : In the formation of $[\text{Fe}(\text{NH}_3)_6]^{3+}$, Fe^{3+} ion provides six vacant orbitals.

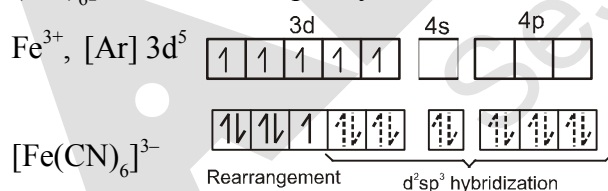
In $[\text{Cu}(\text{NH}_3)_4]^{2+}$, Cu^{+2} ion provides four vacant orbitals.

- The metal provides vacant orbitals only after the process of hybridisation, thus vacant hybrid orbitals are provided by the metal ion.
- The vacant hybrid orbitals of metal ion get overlapped by orbitals of ligands containing lone pair of electrons.
- The number of such overlappings is equal to the coordination number of metal ion.
- The empty 'd' orbitals involved in hybridisation may be inner (n-1)d or outer "nd" orbitals and accordingly complexes are called as **Inner orbital complexes** and **outer orbital complexes** respectively.
- In certain complexes pairing of electrons takes place in ligand field, resulting in decrease in spin only magnetic moment, such complexes are known as Low spin complexes
- Bohr magneton = $\frac{eh}{4\pi mc}$
- Paramagnetism is represented in the term of spin only magnetic moment.

$$\mu = \sqrt{n(n+2)} \text{ B.M.} \quad n = \text{Number of unpaired electron}$$

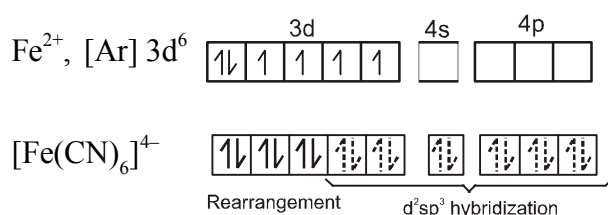
Example $[\text{Fe}(\text{CN})_6]^{3-}$ is weakly paramagnetic while $[\text{Fe}(\text{CN})_6]^{4-}$ is diamagnetic.

Sol. $[\text{Fe}(\text{CN})_6]^{3-}$ involves d^2sp^3 hybridization.



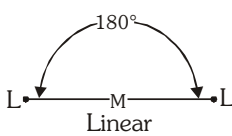
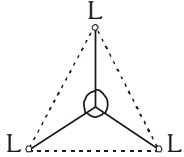
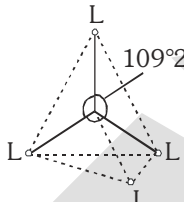
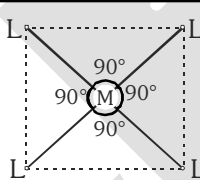
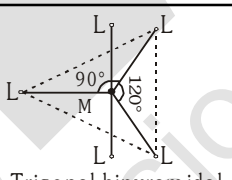
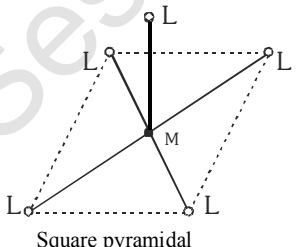
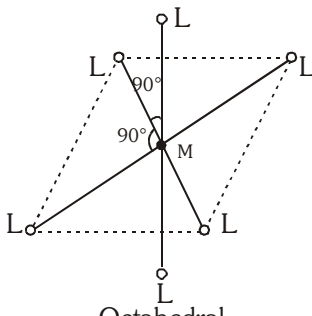
One d-orbital is singly occupied, hence it is weakly paramagnetic in nature.

$[\text{Fe}(\text{CN})_6]^{4-}$ also involves d^2sp^3 hybridization but it has Fe^{2+} ion as central ion.



All electrons are paired, hence it is diamagnetic in nature.

Some Example :

Coordination Number	Hybridised orbitals	Geometrical shape of the Complex	Examples of Complex
2	sp	 Linear	$[\text{Ag}(\text{NH}_3)_2]^+$ $[\text{Ag}(\text{CN})_2]^-$
3	sp^2		$[\text{HgI}_3]^-$
4	sp^3	 $109^\circ 28'$	$[\text{CuCl}_4]^{2-}$ $[\text{ZnCl}_4]^{2-}$ $[\text{FeCl}_4]^-$ $[\text{Ni}(\text{CO})_4]$ $[\text{Zn}(\text{NH}_3)_4]^{+2}$
4	dsp^2 ($d = d_{x^2-y^2}$)	 Square planar	$[\text{PdCl}_4]^{2-}$ $[\text{Ni}(\text{CN})_4]^{2-}$ $[\text{Pt}(\text{NH}_3)_4]^{+2}$ $[\text{Cu}(\text{NH}_3)_4]^{+2}$ $[\text{PtCl}_4]^{2-}$
5	sp^3d ($d = d_{z^2}$) or dsp^3 ($d = d_{z^2}$)	 Trigonal bipyramidal	$[\text{Fe}(\text{CO})_5]$ $[\text{CuCl}_5]^{3-}$
5	sp^3d ($d = d_{x^2-y^2}$) or dsp^3 ($d = d_{x^2-y^2}$)	 Square pyramidal	$[\text{Ni}(\text{CN})_5]^{3-}$
6	d^2sp^3 (inner orbital complex) or sp^3d^2 (outer orbital complex) in both case d-orbitals are d_{z^2} & $d_{x^2-y^2}$.	 Octahedral	$[\text{Cr}(\text{NH}_3)_6]^{+3}$ $[\text{Ti}(\text{H}_2\text{O})_6]^{+3}$ $[\text{Fe}(\text{CN})_6]^{3-}$ $[\text{Co}(\text{NH}_3)_6]^{+3}$ $[\text{PtCl}_6]^{2-}, [\text{CoF}_6]^{3-}$

♦ **Drawback of valence bond theory :**

- It describes bonding in co-ordination compounds only qualitatively but not account for the relative stabilities for different co-ordination complexes.
- It does not offer any explanation for optical absorption spectra (coloration) of complexes
- It does not describe the detailed magnetic properties of co-ordination compounds.

(D) CRYSTAL FIELD THEORY : The drawbacks of VBT of coordination compounds are, to a considerable extent, removed by the Crystal Field Theory.

The crystal field theory (CFT) is an electrostatic model which considers the metal-ligand bond to be ionic arising purely from electrostatic interaction between the metal ion and the ligand. Ligands are treated as point charges in case of anions or dipoles in case of neutral molecules. The five d-orbitals in an isolated gaseous metal atom/ion have same energy, i.e., they are degenerate. This degeneracy is maintained if a spherically symmetrical field of negative charges surrounds the metal atom/ion. However, when this negative field is due to ligands (either anions or the negative ends of polar molecules like NH_3 and H_2O) in a complex, it becomes asymmetrical and the degeneracy of the d orbitals is lost. It results in splitting of the d orbitals. The pattern of splitting depends upon the nature of the crystal field.

(a) Crystal field splitting in octahedral coordination entities :

In an octahedral coordination entity with six ligands surrounding the metal atom/ion, there will be repulsion between the electrons in d orbitals of metal and the electrons (or negative charges) of the ligands. Such a repulsion is more when the d orbitals of metal are directed towards the ligand than when it is away from the ligand.

Thus, the $d_{x^2-y^2}$ and d_{z^2} orbitals (axial orbitals) which point towards the axis along the direction of the ligand will experience more repulsion and will be raised in energy ; and the d_{xy} , d_{yz} and d_{zx} orbitals (non-axial) orbitals which are directed between the axis will be lowered in energy relative to the average energy in the spherical crystal field.

Thus, the degeneracy of the d orbitals has been removed due to ligand electron-metal electron repulsions in the octahedral complex to yield three orbitals of lower energy, t_{2g} set and two orbitals of higher energy, e_g set. This splitting of the degenerate levels due to the presence of ligands in a definite geometry is termed as crystal field splitting and the energy separation is denoted by Δ_0 (the subscript o is for octahedral). Thus, the energy of the two e_g orbitals will increase by $(3/5)\Delta_0$ and that of the three t_{2g} will decrease by $(2/5)\Delta_0$.

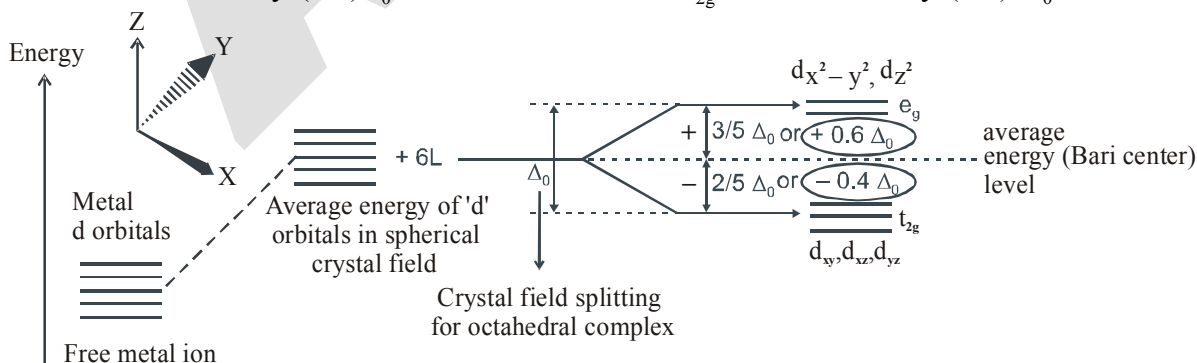


Figure showing crystal field splitting in octahedral complex.

The crystal field splitting, Δ_0 , depends upon the fields produced by the ligand and charge on the metal ion. Some ligands are able to produce strong fields in which case, the splitting will be large whereas others produce weak fields and consequently result in small splitting of d orbitals. In general, ligands can be arranged in a series in the order of increasing field strength as given below :



Note : In SCN^- , S is donating atom and in NCS^- , N is donating atom.

Such a series is termed as spectrochemical series. It is an experimentally determined series based on the absorption of light by complexes with different ligands. For d^4 configuration, the fourth electron will singly occupy e_g orbital (according to Hund's rule) or will undergo pairing in t_{2g} orbital, which of these possibilities occurs, depends on the relative magnitude of the crystal field splitting, Δ_0 and the pairing energy, P (P represents the energy required for electron pairing in a single orbital). The two possibilities are :

- (i) If $\Delta_0 < P$, the fourth electron enters in one of the e_g orbitals giving the configuration $t_{2g}^3 e_g^1$. Ligands for which $\Delta_0 < P$ are known as weak field ligands and form high spin complexes.
- (ii) If $\Delta_0 > P$, it becomes more energetically favourable for the fourth electron to occupy a t_{2g} orbital with configuration $t_{2g}^4 e_g^0$. Ligands which produce this effect are known as strong field ligands and form low spin complexes.

Crystal Field stabilising energy in Octahedral field :

Formula : $\text{CFSE} = [-0.4 n_{t_{2g}} + 0.6 n_{e_g}] \Delta_0 + xP$.

Where $n_{t_{2g}}$ & n_{e_g} are number of electron(s) in t_{2g} & e_g orbitals respectively and Δ_0 crystal field splitting energy for octahedral complex. "x" represents the number of electron pairs and P is mean pairing energy.

(b) Crystal field splitting in tetrahedral coordination entities :

In tetrahedral coordination entity formation, the d orbital splitting is inverted and is smaller as compared to the octahedral field splitting. For the same metal, the same ligands and metal-ligand distances, it can be shown that $\Delta_t = (4/9)\Delta_0$. This may be attributed to the following two reasons.

- (i) There are only four ligands instead of six, so the ligand field is only two thirds the size ; as the ligand field splitting is also the two thirds the size and (ii) the direction of the orbitals does not coincide with the direction of the ligands. This reduces the crystal field splitting by roughly further two third. So $\Delta_t = \frac{2}{3} \times \frac{2}{3} = \frac{4}{9} \Delta_0$.

Consequently, the orbital splitting energies are not sufficiently large for forcing pairing and, therefore, low spin configurations are rarely observed.

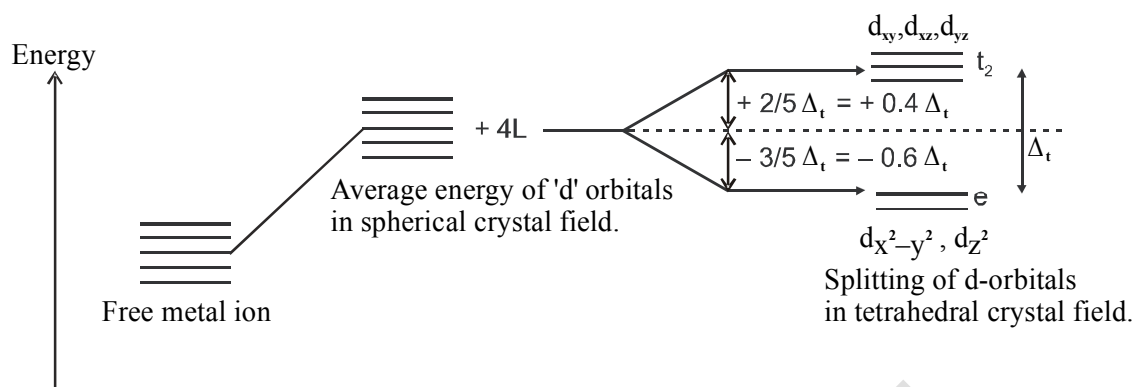


Figure showing crystal field splitting in tetrahedral complex.

Since $\Delta_t < \Delta_o$ crystal field splitting favours the formation of octahedral complexes.

Crystal Field stabilising energy in Tetrahedral field :

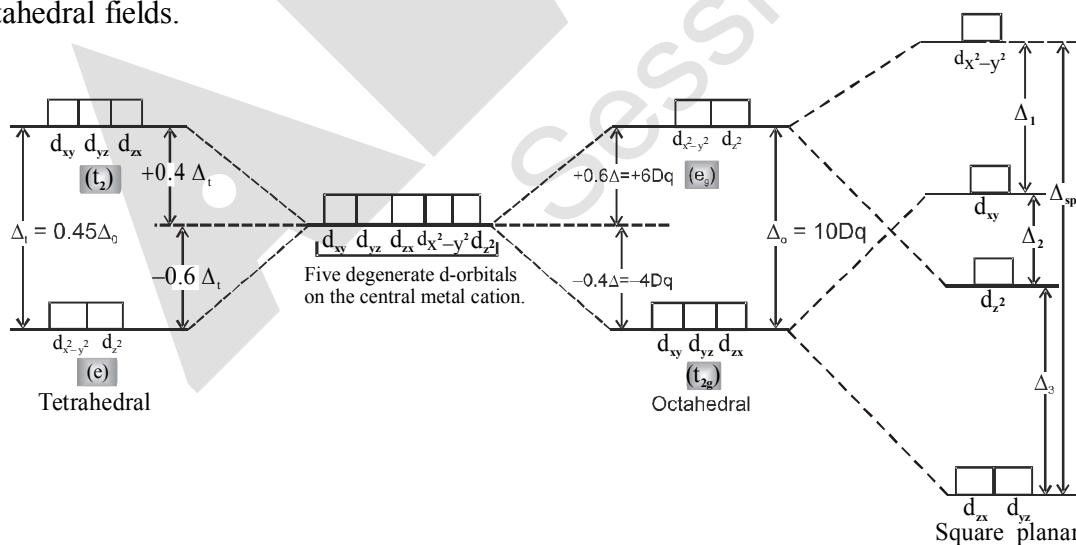
Formula : $CFSE = [-0.6 n_e + 0.4 n_{t_2}] \Delta_t + xP$.

where n_{t_2} & n_e are number of electron(s) in t_2 & e orbitals respectively and Δ_t crystal field splitting energy for tetrahedral complex. "x" represents the number of electron pairs and P is mean pairing energy.

(c) Crystal field splitting in square planar co-ordination entities :

The square planar arrangement of ligands may be considered to be one derived from the octahedral field by removing two trans-ligands located along the Z-axis. In the process, the e_g and t_{2g} sets of orbitals is lifted i.e., these orbitals will no longer be degenerate.

The four ligands in square planar arrangement around the central metal ion are shown in Fig. As the ligands approach through the x and y axis, they would have greatest influence on $d_{x^2-y^2}$ orbital, so the energy of this orbital, will be raised most. The d_{xy} orbital, lying in the same plane, but between the ligands will also have a greater energy though the effect will be less than that on the $d_{x^2-y^2}$ orbitals. On the other hand, due to absence of ligands along Z-axis, the d_{z^2} orbital becomes stable and has energy lower than that of d_{xy} orbital. Similarly d_{yz} and d_{zx} become more stable. The energy level diagram may be represented as shown in figure along with tetrahedral and octahedral fields.



The value of Δ_{sp} has been found larger than Δ_o because of the reason that d_{xz} and d_{yz} orbitals interact with only two ligands in the square planar complexes, while in octahedral complexes the interaction takes place only with four ligands. Δ_{sp} has been found equal to $1.3 \Delta_o$. Thus,

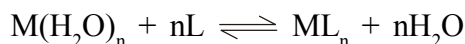
$$\Delta_{sp} = (\Delta_1 + \Delta_2 + \Delta_3) > \Delta_o \quad \text{and} \quad \Delta_{sp} = 1.3 \Delta_o.$$

(E). STABILITY OF COORDINATION COMPOUNDS :

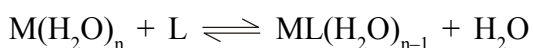
The stability of a coordination compound $[ML_n]$ is measured in terms of the stability constant (equilibrium constant) given by the expression,

$$\beta_n = [ML_n] / [M(H_2O)_n][L]^n$$

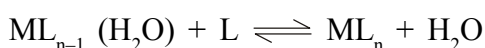
for the overall reaction :



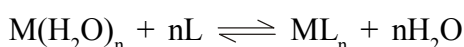
By convention, the water displaced is ignored, as its concentration remains essentially constant. The above overall reaction takes place in steps, with a stability (formation) constant, K_1 , K_2 , K_3 , K_n for each step as represented below :



$$K_1 = [ML(H_2O)_{n-1}] / \{[M(H_2O)_n][L]\}$$



$$K_n = [ML_n] / \{[ML_{n-1}(H_2O)][L]\}$$



$$\beta_n = K_1 \times K_2 \times K_3 \times \dots \times K_n$$

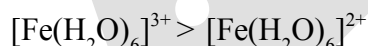
β_n , the stability constant, is related to thermodynamic stability when the system has reached equilibrium. Most of the measurements have been made from aqueous solutions, which implies that the complex is formed by the ligand displacing, water from the aqua complex of the metal ion. Ignoring the charge and taking L as an unidentate ligand, the stepwise formation of the complex is represented as shown above.

K_1 , K_2 , K_3 K_n representing the stepwise stability (or formation) constants.

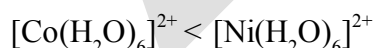
The above is thermodynamic stability criteria, there can be another kind of stability called kinetic stability, which measures the rate of ligand replacement.

(F). FACTORS INFLUENCING THE MAGNITUDE OF C.F.S.E. :

- 1. Different charges on the cation of the same metal :** The cation with a higher oxidation state has a larger value of CFSE than that with lower oxidation state e.g.,



- 2. Same charges on the cation but the number of d-electrons is different :** The metal cation the magnitude of CFSE with the increase of the number of d-electrons, e.g.,



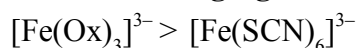
- 3. Quantum number (n) of the d-orbitals of the central metal ion :** As 'n' increase CFSE increases.



- 4. Types of Hybridisation :**

$$\Delta_t = \frac{4}{9} \Delta_o$$

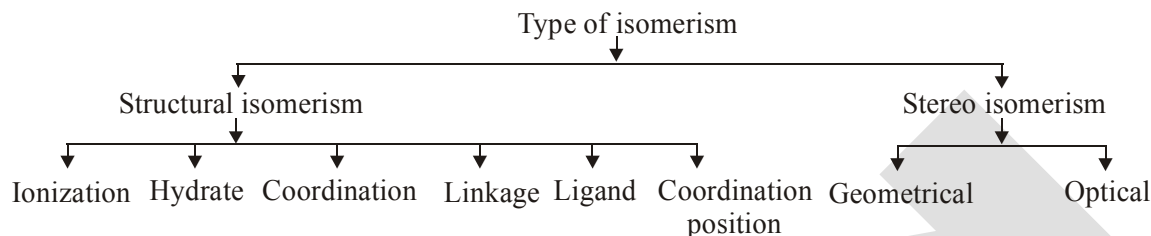
- 5. Presence of cheleting ligand increases CFSE :**



□ ISOMERISM IN COMPLEXES

- (a) Compounds which have the same molecular formula, but differ in their properties due to the difference in structure are called as **Isomers**.
- (b) Isomerism is commonly considered, to be the characteristic of only organic compounds, it is also found although less frequently among inorganic substances.

❖ CLASSIFICATION OF ISOMERISM



(A) Structural isomerism

It arises due to the difference in the type of chemical linkages and distribution of ligands within and outside the coordination sphere.

(a) Ionisation isomerism

The type of isomerism which is due to the exchange of groups or ions between the coordination sphere and the ionisation sphere.

Example. (i) $\text{Co}(\text{NH}_3)_4\text{Br}_2\text{SO}_4$ can be represented as
 $[\text{Co}(\text{NH}_3)_4\text{Br}_2]\text{SO}_4$ (red violet) and $[\text{Co}(\text{NH}_3)_4\text{SO}_4]\text{Br}_2$ (red)
 These complexes give sulphate ion and bromide ion respectively

(ii) $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Br}_2$ and $[\text{Pt}(\text{NH}_3)_4\text{Br}_2]\text{Cl}_2$

(iii) $[\text{Co}(\text{NH}_3)_4(\text{NO}_3)_2]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_4\text{SO}_4](\text{NO}_3)_2$

(b) Hydrate isomerism

This type of isomerism is due to presence of different number of water molecules inside a coordination sphere.

Example. $\text{Cr}(\text{H}_2\text{O})_6\text{Cl}_3$ has four possible structures

(i) $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ violet

(ii) $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ green

(iii) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ dark green.

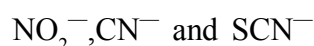
(iv) $[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3] \cdot 3\text{H}_2\text{O}$ dark green.

These complexes differ from one another with respect to the number of water molecules acting as ligands. Other hydrate isomers are

$[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl} \cdot \text{H}_2\text{O}$

(c) Linkage isomerism

(i) This type of isomerism arises due to presence of ambidentate ligands like



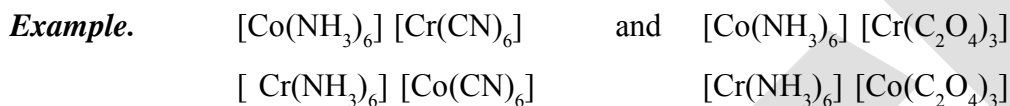
(ii) These ligands have two donor atoms but at a time only one atom is directly linked to the central metal atom of the complex.

(iii) Such type of isomers are distinguished by infra red (I.R.) spectroscopy.

- Example.**
- $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$
 - In NO_2^- ligand, The coordinating sites are nitrogen (i.e., NO_2^- Nitro ligand) or through oxygen (i.e. ONO Nitrito ligand)
 - The nitro isomer is yellow and is stable to acids whereas nitrito isomer is red and is decomposed by acids.

(d) **Coordination isomerism**

- This type of isomerism is exhibited when the complex has two complex ions in it - 'cationic and anionic'.
- This type of isomerism is caused by the interchange of ligands between the two complex ions of the same complex.



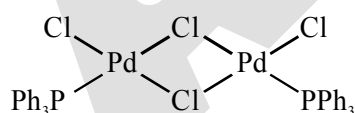
(e) **Ligand isomerism**

- Ligands with $\text{C}_3\text{H}_6(\text{NH}_2)_2$ have two different structures i.e. 1, 3-diamino propane and 1, 2-diaminopropane(propylene diamine).
- Those complexes which have same molecular formula, but differ with respect to their ligands are called as **Ligand isomers**.

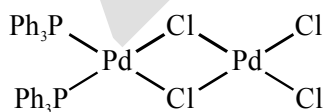


(f) **Co-ordination Position Isomerisation :**

It is shown by polynuclear complexes, due interchange of ligands between the different metal nuclei.

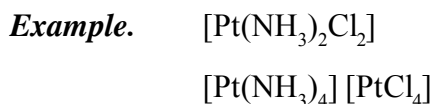


Example.



(g) **Polymerization Isomerism :**

This is not true isomerism because it occurs between compounds having the same empirical formula, but different molecular weights.



(B) Stereo isomerism

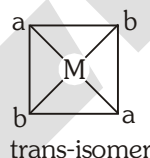
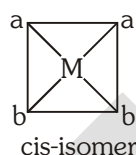
They have same molecular formula, same constitution, they differ only with respect to the spatial orientation of ligands in space around the metal ion. The two stereo isomers which are possible Geometrical and Optical.

(a) Geometrical isomerism

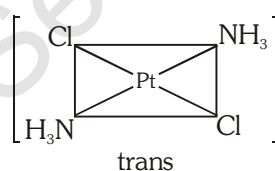
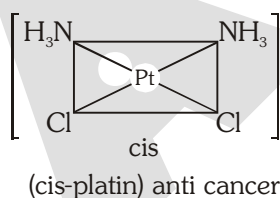
- (i) The ligands occupy different positions around the central metal ion.
- (ii) When two identical ligands are co-ordinated to the metal ion from same side then it is **cis isomer**. (Latin, cis means same).
- (iii) If the two identical ligands are co-ordinated to the metal ion from opposite side then it is **trans isomer** (in Latin, trans means across).

Geometrical isomers with co-ordination number = 4 (Square planar complexes)

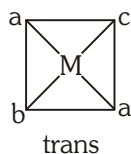
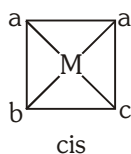
- (i) Complexes with general formula, Ma_2b_2 (where both a and b are monodentate) can have cis-and trans isomers.



Example.



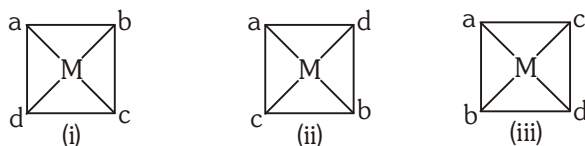
- (ii) Complexes with general formula Ma_2bc can have cis - and trans-isomers.



Example. $[\text{Pt}(\text{NH}_3)_2\text{ClBr}]$



(iii) Complexes with general formula, $\text{Ma}_2\text{b}_2\text{cd}$ can have three isomers.



Geometrical isomers with Co-ordination number = 6

(i) Complexes with general formula Ma_4b_2 can have cis - and trans-isomers.

Example. $[\text{Fe}(\text{NH}_3)_4\text{Cl}_2]$



(iii) **Facial and Meridional isomerism (Ma_3b_3)**



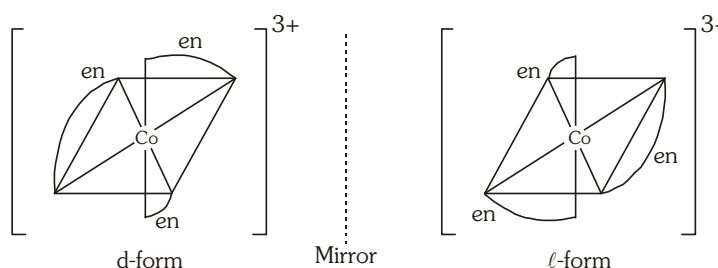
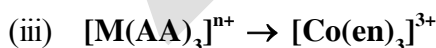
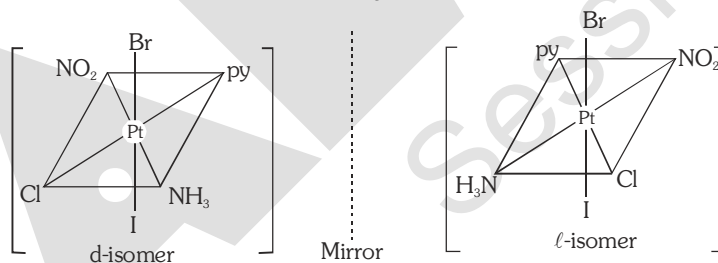
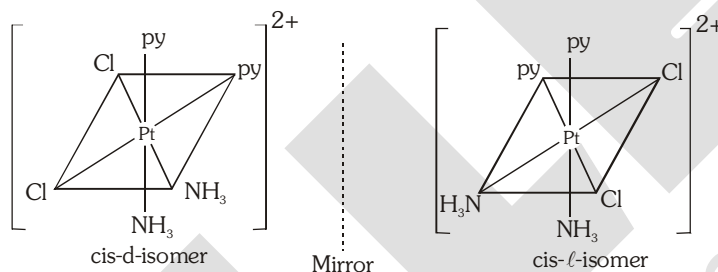
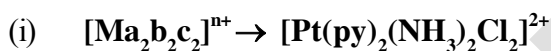
Other 6-Coordinated geometrical isomers are

Note :	General formula	Total No. of geometrical isomers
	Mabcdef	15
	Ma_2bcde	9
	$\text{Ma}_2\text{b}_2\text{cd}$	6
	$\text{Ma}_2\text{b}_2\text{c}_2$	5
	Ma_3bcd	4
	$\text{Ma}_3\text{b}_2\text{c}$	3
	Ma_3b_3	2
	Ma_4bc	2
	Ma_4b_2	2
	Ma_5b	Not possible
	Ma_6	Not possible

Here M = central atom a, b, c, d, e, f = Monodentate ligands

(b) **Optical isomers**

- (i) Optically active complexes are those which are nonsuperimposable over the mirror image structure.
- (ii) An optically active complex is one which is asymmetric in nature i.e., not divisible into two identical halves.
- (iii) The complex which rotates plane polarised light to left hand side is **laevo rotatory** i.e. '*l*' or '-' and if the complex rotates the plane polarised light to right hand side then it is **dextro rotatory** '*d*' or '+'.
 - (iv) Thus complexes which have same physical and chemical properties but differ in their action towards plane polarised light are called as **optical isomers**.
 - (v) The '*d*' and '*l*' isomers of a compound are called as **Enantiomers or Enantiomorphs**.
 - (vi) Optical isomerism is expected in tetrahedral complexes of the type $Mabcd$.

Optical isomers with Co-ordination number = 6

NUMBER OF POSSIBLE ISOMERS FOR SPECIFIC COMPLEXES

Formula	Number of stereoisomers	Pairs of Enantiomers
$M_{a_4b_2}$	2	0
$M_{a_3b_3}$	2	0
M_{a_4bc}	2	0
M_{a_3bcd}	5	1
M_{a_2bcde}	15	6
M_{abcdef}	30	15
$M_{a_2b_2c_2}$	6	1
$M_{a_2b_2cd}$	8	2
$M_{a_3b_2c}$	3	0
$M(AA)(BC)de$	10	5
$M(AB)(AB)cd$	11	5
$M(AB)(CD)ef$	20	10
$M(AB)_3$	4	2

Note : Uppercase letters represent chelating ligands and lowercase letters represent monodentate ligands.

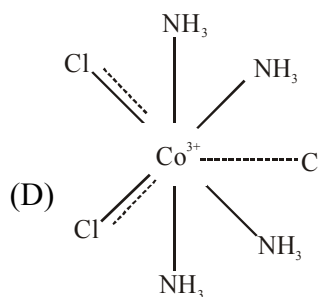
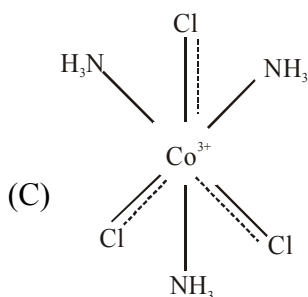
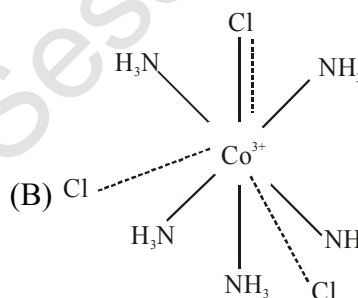
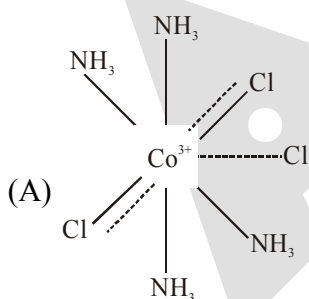
EXERCISE # O-1

SINGLE OPTION CORRECT :*Double salt and complex compound*

- Some salts although containing two different metallic elements give test for one of them in solution. Such salts are
(A) complex salt (B) double salt (C) normal salt (D) none of these
- Aqueous solution of FeSO_4 gives tests for both Fe^{2+} and SO_4^{2-} but after addition of excess of KCN, solution ceases to give test for Fe^{2+} . This is due to the formation of
(A) the double salt $\text{FeSO}_4 \cdot 2\text{KCN} \cdot 6\text{H}_2\text{O}$ (B) $\text{Fe}(\text{CN})_3$
(C) the complex ion $[\text{Fe}(\text{CN})_6]^{4-}$ (D) the complex ion $[\text{Fe}(\text{CN})_6]^{3-}$

Werner theory

- Consider the following statements:
According to the Werner's theory.
(a) Ligands are connected to the metal ions by covalent bonds.
(b) Secondary valencies have directional properties
(c) Secondary valencies are non-ionisable
Of these statements:
(A) a, b and c are correct (B) b and c are correct
(C) a and c are correct (D) a and b are correct
- A complex of platinum, ammonia and chloride produces four ions per molecule in the solution. The structure consistent with the observation is:
(A) $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_4$ (B) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$ (C) $[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Cl}_3$ (D) $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2$
- Which of the following Werner's complex has least electrical conductivity ?



Classification of ligand

6. How many EDTA^{4-} molecules are required to make an octahedral complex with a Ca^{2+} ion ?
(A) Six (B) Three (C) One (D) Two
7. π -bonding is not involved in :
(A) ferrocene (B) dibenzene chromium (C) Zeise's salt (D) Grignard reagent
8. Which of the following is not considered as an organometallic compound ?
(A) Ferrocene (B) Cis-platin (C) Ziese's salt (D) Grignard reagent
9. Diethylene triamine is:
(A) Chelating agent (B) Polydentate ligand
(C) Tridentate ligand (D) All of these
10. Which of the following species is not expected to be a ligand
(A) NO^+ (B) NH_4^+ (C) $\text{NH}_2\text{--NH}_3^+$ (D) CO
11. The disodium salt of ethylene diamine tetraacetic acid can be used to estimate the following ion(s) in the aqueous solution
(A) Mg^{2+} ion (B) Ca^{2+} ion (C) Na^+ ion (D) both Mg^{2+} and Ca^{2+}
12. Which of the following ligand does not act as bidentate ligand
(A) dipy (B) dien (C) gly⁻ (D) dmg⁻

Synergic bonding

13. Which of the following order is correct for the IR vibrational frequency of CO.
(A) $[\text{Fe}(\text{CO})_4]^{2-} < [\text{Co}(\text{CO})_4]^- < [\text{Ni}(\text{CO})_4]$ (B) $[\text{Fe}(\text{CO})_4]^{2-} > [\text{Co}(\text{CO})_4]^- > [\text{Ni}(\text{CO})_4]$
(C) $[\text{Fe}(\text{CO})_4]^{2-} > [\text{Co}(\text{CO})_4]^- < [\text{Ni}(\text{CO})_4]$ (D) $[\text{Fe}(\text{CO})_4]^{2-} < [\text{Co}(\text{CO})_4]^- > [\text{Ni}(\text{CO})_4]$
14. In the isoelectronic series of metal carbonyl, the C–O bond strength is expected to increase in the order.
(A) $[\text{Mn}(\text{CO})_6]^+ < [\text{Cr}(\text{CO})_6] < [\text{V}(\text{CO})_6]^-$ (B) $[\text{V}(\text{CO})_6]^- < [\text{Cr}(\text{CO})_6] < [\text{Mn}(\text{CO})_6]^+$
(C) $[\text{V}(\text{CO})_6]^- < [\text{Mn}(\text{CO})_6]^+ < [\text{Cr}(\text{CO})_6]$ (D) $[\text{Cr}(\text{CO})_6] < [\text{Mn}(\text{CO})_6]^+ < [\text{V}(\text{CO})_6]^-$
15. Which of the following has higher stretching frequency for C–O bond -
(A) $[\text{Ni}(\text{CO})_3\text{PF}_3]$ (B) $[\text{Ni}(\text{CO})_3(\text{PMe}_3)]$
(C) both have equal stretching frequency (D) None of these
16. Which of the following has higher multiple bond character in M–C bond -
(A) $[\text{Ni}(\text{CO})_4]$
(B) $[\text{Co}(\text{CO})_4]^-$
(C) $[\text{Fe}(\text{CO})_4]^{2-}$
(D) (B) and (C) both have equal multiple bond character in M–C bond
17. The V–C distance in $\text{V}(\text{CO})_6$ and $[\text{V}(\text{CO})_6]^-$ are respectively (in pm)-
(A) 200, 200 (B) 193, 200 (C) 200, 193 (D) 193, 193

Co-ordination number and E.A.N.

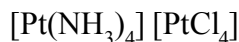
18. Among the following complexes which can act as oxidising agent.
 (A) $[\text{Mn}(\text{CO})_6]$ (B) $[\text{Mn}(\text{CO})_6]^+$ (C) $[\text{Mn}(\text{CO})_5]^-$ (D) $[\text{V}(\text{CO})_6]$
19. Which of the following statement is correct regarding the compound " $[(\text{CO})_3\text{Fe}(\text{CO})_3\text{Fe}(\text{CO})_3]$ ".
 (A) The $d_{\text{C-O}}$ (bridging) is greater than $d_{\text{C-O}}$ (terminal)
 (B) The bond order of bridging C – O bond is greater than that of terminal C – O bond
 (C) The E.A.N. value of each Fe-atom is 35
 (D) The oxidation state of Fe in this complex is (–I)
20. How many π electrons are donated by C_5H_5^- ligand -
 (A) 2 (B) 4 (C) 5 (D) 6
21. Effective atomic number of $\text{Co}(\text{CO})_4$ is 35, hence it is less stable. It attains stability by
 (A) Oxidation of Co (B) Reduction of Co
 (C) Dimerization (D) Both (B) & (C)
22. In the complex $\text{Fe}(\text{CO})_x$, the value of x is:
 (A) 3 (B) 4 (C) 5 (D) 6
23. The EAN of platinum in potassium hexachloroplatinate (IV) is:
 (A) 46 (B) 86 (C) 36 (D) 84
24. The EAN of metal atoms in $\text{Fe}(\text{CO})_2(\text{NO})_2$ and $\text{Co}_2(\text{CO})_8$ respectively are
 (A) 34, 35 (B) 34, 36 (C) 36, 36 (D) 36, 35

Naming of complex compound

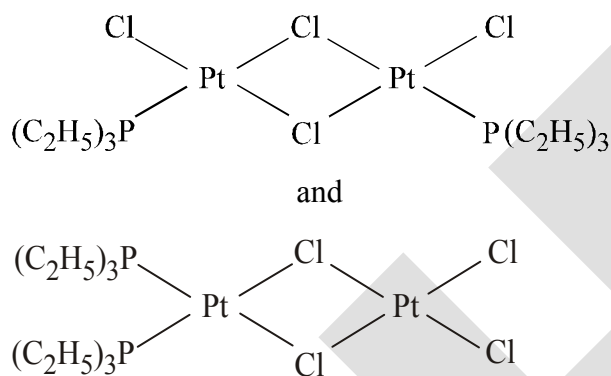
25. The IUPAC name for the coordination compound $\text{Ba}[\text{BrF}_4]_2$ is
 (A) Barium tetrafluorobromate (V) (B) Barium tetrafluorobromate (III)
 (C) Barium bis (tetrafluorobromate) (III) (D) none of these
26. The number of ions formed, when bis (ethane-1,2-diamine) copper (II) sulphate is dissolved in water will be
 (A) 1 (B) 2 (C) 3 (D) 4
27. The IUPAC name of the Wilkinson's catalyst $[\text{Rh Cl}(\text{P Ph}_3)_3]$ is
 (A) Chloridotris(triphenylphosphine)rhodium(I)
 (B) Chloridotris(triphenylphosphine)rhodium(IV)
 (C) Chloridotris(triphenylphosphine)rhodium(0)
 (D) Chloridotris(triphenylphosphine)rhodium(VI)
28. The formula for the compound tris (ethane-1, 2-diamine)cobalt (III) sulphate is
 (A) $[\text{Co}(\text{en})_3]\text{SO}_4$ (B) $[\text{Co}(\text{SO})_4(\text{en})_3]$
 (C) $[\text{Co}(\text{en})_3](\text{SO}_4)_2$ (D) $[\text{Co}(\text{en})_3]_2(\text{SO}_4)_3$

Structural isomerism

29. Which of the following statement is **INCORRECT** regarding the following compound



- (A) It is the polymerisation isomer of $[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]$
 (B) E.A.N. of cationic part is equal to that of anionic part
 (C) It is the co-ordination isomer of $[\text{Pt}(\text{NH}_3)_3\text{Cl}][\text{Pt}(\text{NH}_3)\text{Cl}_3]$
 (D) Synergic bonding is not involved in the complex
30. The type of isomerism present in pentaamminenitrochromium (III) chloride is :
 (A) optical (B) linkage (C) hydrate (D) polymerisation
31. The complexes given below show:



- (A) Optical isomerism (B) Co-ordination isomerism
 (C) Geometrical isomerism (D) Co-ordination position isomerism
32. Which of the following complex shows ionization isomerism
 (A) $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$ (B) $[\text{Cr}(\text{en})_2]\text{Cl}_2$
 (C) $[\text{Cr}(\text{en})_3]\text{Cl}_3$ (D) $[\text{CoBr}(\text{NH}_3)_5]\text{SO}_4$
33. Find the name of the hydrate isomer of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, which is having lowest electrical conductivity excluding zero value of conductivity.
 (A) Hexaaquachromium(III) chloride
 (B) Tetraaquadichloridochromium(III) chloride dihydrate
 (C) Pentaquachloridochromium(III) chloride monohydrate
 (D) Triaquatrichloridochromium(III) chloride trihydrate

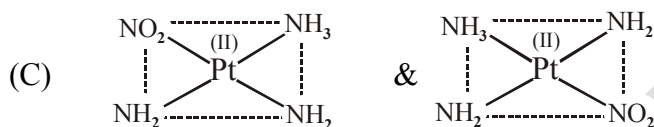
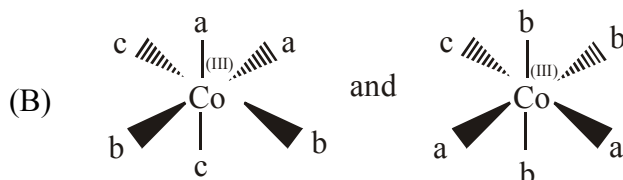
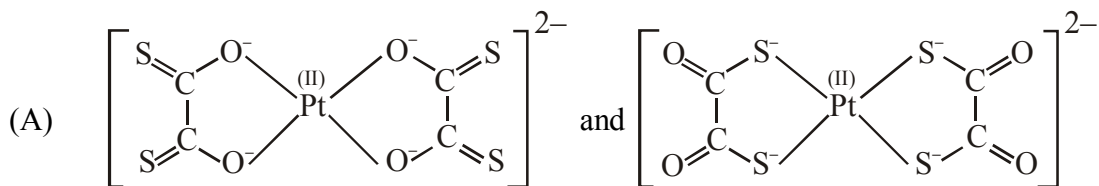
Stereoisomerism

34. Which of the following complex shows optical isomerism -
 (A) $[\text{Cd}(\text{CN})_4]^{2-}$ (B) $[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3] \cdot 3\text{H}_2\text{O}$
 (C) $[\text{Zn}(\text{gly})_2]^0$ (D) $[\text{Ni}(\text{dmg})_2]^0$

35. How many coordination isomers of $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$ show geometrical isomerism.

- (A) All (B) One (C) Two (D) None

36. Identify the pair of complex which are stereoisomer of each other -



(D) All of the above

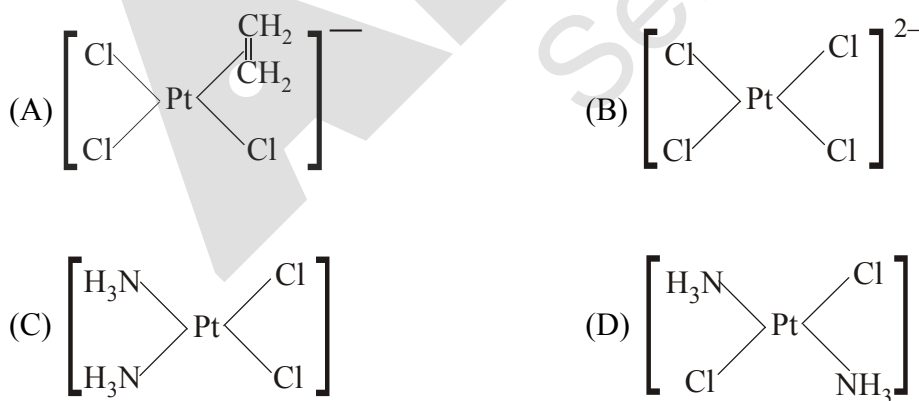
37. Find complex which have maximum number of stereoisomers -

- (A) $[\text{Ma}_3\text{b}_3]$ (B) $[\text{Ma}_3\text{b}_2\text{c}]$ (C) $[\text{Ma}_2\text{b}_2\text{c}_2]$ (D) $[\text{M}(\text{AA})_2\text{a}_2\text{b}_2]$

38. In which of the following pairs both the complexes show optical isomerism ?

- (A) $\text{cis}-[\text{Cr}(\text{C}_2\text{O}_4)_2\text{Cl}_2]^{3-}$, $\text{trans}-[\text{Co}(\text{NH}_3)_4\text{Cl}_2]$
 (B) $[\text{Co}(\text{en})_3]\text{Cl}_3$, $\text{cis}-[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$
 (C) $[\text{PtCl}(\text{dien})]\text{Cl}$, $[\text{NiCl}_2\text{Br}_2]^{2-}$
 (D) $[\text{Co}(\text{NO}_3)_3(\text{NH}_3)_3]$, $\text{cis}-[\text{Pt}(\text{en})_2\text{Cl}_2]$

39. Which of the following is considered to be an anticancer species ?



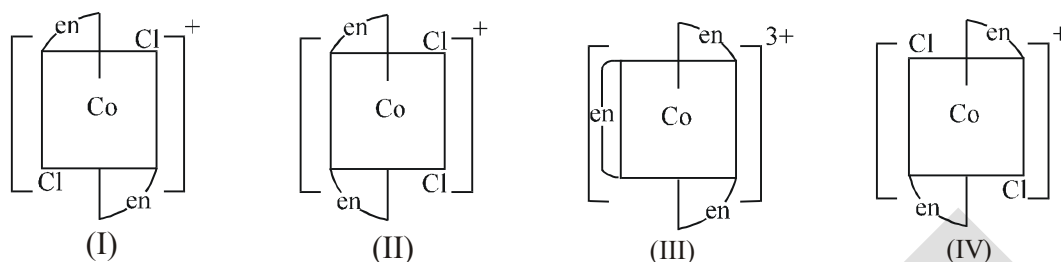
40. Which of the following can exhibit geometrical isomerism ?

- (A) $[\text{MnBr}_4]^{2-}$ (B) $[\text{Pt}(\text{NH}_3)_3\text{Cl}]^+$
 (C) $[\text{PtCl}_2(\text{P}(\text{C}_2\text{H}_5)_3)_2]$ (D) $[\text{Fe}(\text{H}_2\text{O})_5\text{NOS}]^{2+}$

41. The oxidation state of Mo in its oxo-complex species $[\text{Mo}_2\text{O}_4(\text{C}_2\text{H}_4)_2(\text{H}_2\text{O})_2]^{2-}$ is:

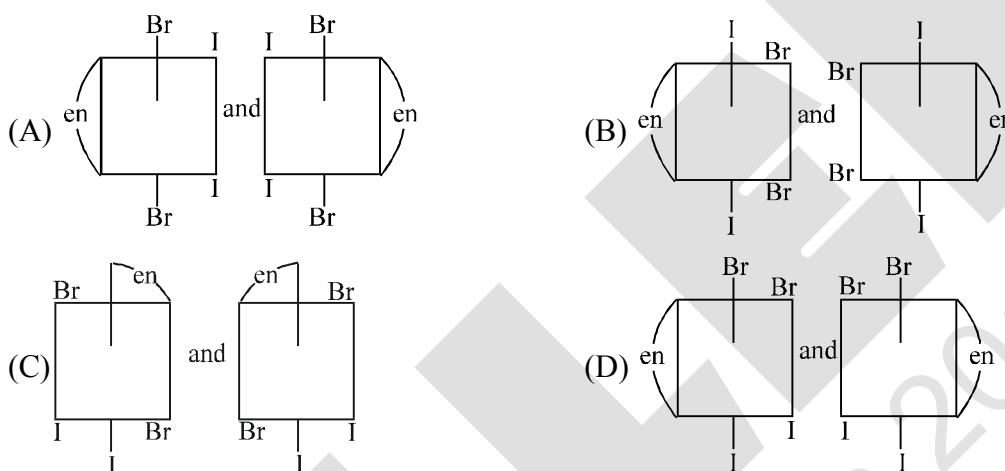
- (A) +2 (B) +3 (C) +4 (D) +5

42. Which of the following ions are optically active?



- (A) I only (B) II only (C) II and III (D) IV only

43. The complex ion has two optical isomers. Their **CORRECT** configurations are:



V.B.T/CFT

44. Which of the following complex is coloured and diamagnetic -

- (A) MnO_4^{2-} (B) $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ (C) $[\text{CrCl}_6]^{3-}$ (D) CrO_4^{2-}

45. What is the hybridisation of Fe in $[\text{Fe}(\text{CO})_4]^{-2}$

- (A) d^2sp^3 (B) sp^3d^2 (C) sp^3d (D) sp^3

46. One unknown complex has the spin only magnetic moment is of 1.73 BM. As per the C. F. T., complex is.

- (A) d^7 , Oh-field, with Strong Field Ligand (B) d^9 , sq.planar-field, with Strong Field Ligand
(C) d^9 , Td, field with Weak Field Ligand (D) All of these

47. Identify tetrahedral species which has maximum magnetic moment value :

- (A) $[\text{CuCl}_4]^{2-}$ (B) $[\text{CoCl}_4]^{2-}$ (C) $[\text{FeCl}_4]^{2-}$ (D) $[\text{AlCl}_4]^-$

48. In the co-ordination compound $\text{Na}_4[\text{Fe}(\text{CN})_5\text{NOS}]$ oxidation state of Fe is -

- (A) +1 (B) +2 (C) +3 (D) +4

49. Which one of the following complex is an outer orbital complex -

- (A) $[\text{Ni}(\text{H}_2\text{O})_6]^{+2}$ (B) $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$
(C) $[\text{Fe}(\text{NH}_3)_6]^{+2}$ (D) All of these

50. Which of the following is diamagnetic and sp^3 hybridised -
 (A) $[\text{NiCl}_4]^{2-}$ (B) $[\text{Ni}(\text{CN})_4]^{4-}$ (C) $[\text{Ni}(\text{CN})_4]^{2-}$ (D) $[\text{NiCl}_2(\text{PPh}_3)_2]$
51. $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ (atomic number of Cr = 24) has a magnetic moment of 3.83 B.M. The **CORRECT** distribution of 3d electrons in the chromium present in the complex is:
 (A) $3d_{xy}^1, 3d_{yz}^1, 3d_{zx}^1$ (B) $3d_{xy}^1, 3d_{yz}^1, 3d_{z^2}^1$
 (C) $3d_{(x^2-y^2)}^1, 3d_{z^2}^1, 3d_{xz}^1$ (D) $3d_{xy}^1, 3d_{(x^2-y^2)}^1, 3d_{yz}^1$
52. $[\text{Fe}(\text{H}_2\text{O})_6]^{+2}$ has Crystal Field Splitting Energy value $10,400 \text{ cm}^{-1}$ and pairing energy value $17,600 \text{ cm}^{-1}$ then it is :
 (A) Low spin complex (B) Paramagnetic in nature
 (C) Diamagnetic in nature (D) None of these
53. In which of the following coordination entities, the magnitude of Δ_0 [CFSE in octahedral field] will be maximum? :
 (A) $[\text{Co}(\text{CN})_6]^{3-}$ (B) $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$
 (C) $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ (D) $[\text{Co}(\text{NH}_3)_6]^{3+}$
54. The number of unpaired electrons calculated in $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $[\text{CoF}_6]^{3-}$ are :
 (A) 4 and 4 (B) 0 and 2 (C) 2 and 4 (D) 0 and 4
55. An ion M^{2+} , forms the complexes $[\text{M}(\text{H}_2\text{O})_6]^{2+}$, $[\text{M}(\text{en})_3]^{2+}$ and $[\text{MBr}_6]^{4-}$, match the complex with the appropriate colour.
 (A) Green, blue and red (B) Blue, red and green
 (C) Green, red and blue (D) Red, blue and green
56. Formula of ferrocene is:
 (A) $[\text{Fe}(\text{CN})_6]^{4-}$ (B) $[\text{Fe}(\text{CN})_6]^{3+}$ (C) $[\text{Fe}(\text{CO})_5]$ (D) $[\text{Fe}(\text{C}_5\text{H}_5)_2]$
57. $\text{Ni}(\text{CO})_4$ and $[\text{Ni}(\text{NH}_3)_4]^{2+}$ do not differ in
 (A) magnetic moment (B) oxidation number of Ni
 (C) geometry (D) EAN
58. A complex of certain metal has the magnetic moment of 4.91 BM whereas another complex of the same metal with same oxidation state has zero magnetic moment. The metal ion could be
 (A) Co^{2+} (B) Mn^{2+} (C) Fe^{2+} (D) Fe^{3+}
59. The tetrahedral $[\text{CoI}_4]^{2-}$ and square planar $[\text{PdBr}_4]^{2-}$ complex ions are respectively
 (A) low spin, high spin (B) high spin, low spin
 (C) both low spin (D) both high spin
60. Which one of the following species does not represent cationic species of vanadium formed in aqueous solution
 (A) VO_2^+ (B) VO^{2+} (C) $[\text{V}(\text{H}_2\text{O})_6]^{3+}$ (D) VO_2^{2+}

61. On treatment of $[\text{Ni}(\text{NH}_3)_4]^{2+}$ with concentrated HCl , two compounds I and II having the same formula, $[\text{NiCl}_2(\text{NH}_3)_2]$ are obtained, I can be converted into II by boiling with dilute HCl . A solution of I reacts with oxalic acid to form $[\text{Ni}(\text{C}_2\text{O}_4)(\text{NH}_3)_2]$ whereas II does not react. Point out the correct statement of the following
- (A) I cis, II trans; both tetrahedral (B) I cis, II trans; both square planar
(C) I trans, II cis; both tetrahedral (D) I trans, II cis; both square planar
62. Among the following, the compound that is both paramagnetic and coloured is
- (A) $\text{K}_2\text{Cr}_2\text{O}_7$ (B) $(\text{NH}_4)_2[\text{TiCl}_6]$ (C) VOSO_4 (D) $\text{K}_3[\text{Cu}(\text{CN})_4]$
63. The magnetic moment of $[\text{NiX}_4]^{2-}$ ion is found to be zero. Then the metal of the complex ion is (X = monodentate anionic ligand).
- (A) sp^3 hybridised (B) sp^2 hybridised (C) dsp^2 hybridised (D) d^2sp hybridised
64. For which of the following types of d^n configuration, the number of unpaired electrons in octahedral complexes remains same irrespective of the ligand field strength.
- (A) d^3 (B) d^4 (C) d^5 (D) d^6
65. Which of the following electronic arrangement gives the highest value of the magnetic moment?
- (A) d^6 , strong field (B) d^7 , high spin (C) d^4 , weak field (D) d^2 , strong field
66. Select appropriate ligand for given complex
- $[\text{Co}(\text{.....})_6]^{+x}$; $\mu = 0 \text{ BM}$
- (A) $\text{C}_2\text{O}_4^{2-}$ (B) en (C) H_2O (D) F^-
67. According to C.F.T., ligands are treated as -
- (A) Point charges (B) Lewis acids (C) Proton donor (D) All of the above
68. Which of the following is correct electronic configuration of 3d orbital in excited state of central metal ion, when $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ absorbed yellow-green light.
- (A) 3d

			1	
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 (B) t_{2g}^1, e_g^0
(C) t_{2g}^1, e_g^1 (D) t_{2g}^0, e_g^1
69. If $\lambda_{\text{absorbed}}$ for d-d transition is in order $[\text{Ti}(\text{X})_6]^{3+} > [\text{Ti}(\text{Y})_6]^{3+} > [\text{Ti}(\text{Z})_6]^{3+}$.
Select correct order of strength of ligands (X, Y, Z are monodentate ligand)-
- (A) $\text{Z} > \text{Y} > \text{X}$ (B) $\text{X} > \text{Y} > \text{Z}$
(C) $\text{Z} > \text{X} > \text{Y}$ (D) Not predictable

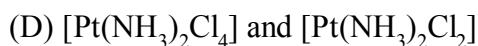
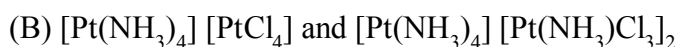
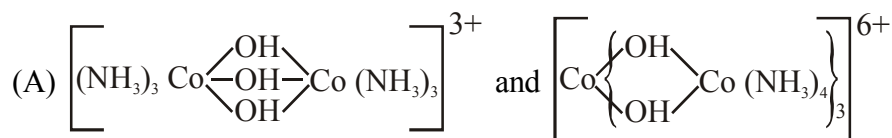
EXERCISE # O-2

MORE THAN ONE MAY BE CORRECT

- Which of the following exhibit geometrical isomerism (M stands for a metal, and a and b are achiral ligands)?
(A) Ma_2b_2 (Sq. Pl.) (B) Ma_4b_2 (C) Ma_5b (D) Ma_6
- Which of the following statement(s) is (are) **CORRECT** ?
(A) The oxidation state of iron in sodium nitroprusside $\text{Na}_2[\text{Fe}(\text{CN})_5(\text{NO})]$ is +II.
(B) $[\text{Ag}(\text{CN})_2]^-$ is linear in shape.
(C) In $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, Fe is d^2sp^3 hybridized.
(D) In $\text{Ni}(\text{CO})_4$, the oxidation state of Ni is zero.
- Which of the following compound(s) show(s) optical isomerism.
(A) $[\text{Pt}(\text{bn})_2]^{2+}$ (B) $[\text{CrCl}_2(\text{en})_2]^+$ (C) $[\text{Co}(\text{en})_3][\text{CoF}_6]$ (D) $[\text{Zn}(\text{gly})_2]$
- Select **INCORRECT** statement(s) for $[\text{Cu}(\text{CN})_4]^{3-}$, $[\text{Cd}(\text{CN})_4]^{2-}$ and $[\text{Cu}(\text{NH}_3)_4]^{2+}$ complex ion.
(A) Both $[\text{Cd}(\text{CN})_4]^{2-}$ and $[\text{Cu}(\text{NH}_3)_4]^{2+}$ have square planar geometry
(B) $[\text{Cu}(\text{CN})_4]^{3-}$ and $[\text{Cu}(\text{NH}_3)_4]^{2+}$ have equal no. of unpaired electron
(C) $[\text{Cu}(\text{CN})_4]^{3-}$ and $[\text{Cd}(\text{CN})_4]^{2-}$ can be separated from the mixture on passing H_2S gas.
(D) All the three complexes have magnetic moment equal to zero.
- Which of the following will have two stereoisomeric forms?
(A) $[\text{Cr}(\text{NO}_3)_3(\text{NH}_3)_3]$ (B) $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$
(C) $[\text{CoCl}_2(\text{en})_2]^+$ (D) $[\text{CoBrCl}(\text{Ox})_2]^{3-}$
- Which is / are **NOT** correctly matched.

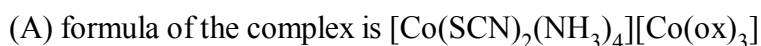
Complex compounds	IUPAC name
(A) $\text{K}[\text{CrF}_4\text{O}]$	Potassium tetrafluoridooxidochromate(V)
(B) $\text{Na}[\text{BH}(\text{OCH}_3)_3]$	Sodium hydridotrimethoxyborate(III)
(C) $[\text{Be}(\text{CH}_3\text{—CO—CH}_2\text{—CO—C}_6\text{H}_5)_2]^\circ$	Bis(benzoylacetato)beryllium(III)
(D) $\text{H}[\text{AuCl}_4]$	Hydrogen tetrachloroaurate(III)
- Which of the following statement(s) is/are **INCORRECT**
(A) In $[\text{CoBrCl}(\text{en})_2]^+$ geometrical isomerism exists, while optical isomerism does not exist
(B) Potassium aquadicyanidosuperoxidoperoxidochromate(III) is IUPAC name for $\text{K}_2[\text{Cr}(\text{CN})_2\text{O}_2(\text{O}_2)(\text{H}_2\text{O})]$
(C) There are 3 geometrical isomers and 15 stereoisomers possible for $[\text{Pt}(\text{NO}_2)(\text{NH}_3)(\text{NH}_2\text{OH})(\text{py})]^+$ and $[\text{PtBrCl}(\text{NO}_2)(\text{NH}_3)(\text{py})]$ respectively
(D) cis and trans forms are not diastereomers of each other

8. Which of the following complexes are polymerisation isomers :



9. Which of the following is **CORRECT** about

Tetraamminedithiocyanato-Scobalt(III) tris(oxalato)cobaltate(III)

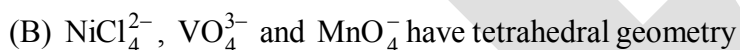
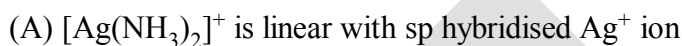


(B) It is a chelating complex and show linkage isomerism.

(C) It shows optical isomerism.

(D) It shows geometrical isomerism.

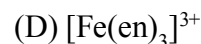
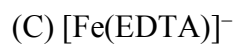
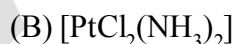
10. Which is **CORRECT** statement(s)?



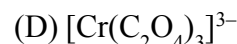
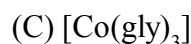
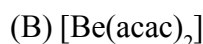
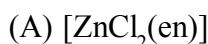
11. In which of the following complex(s) spin only magnetic moment is independent, from the nature of ligand. (L = monodentate ligand) -



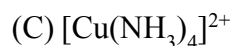
12. Which of the following compound(s) can show optical isomerism ?



13. Which of the following compounds are resolvable into d or ℓ -forms?



14. Which of the following ion is/are diamagnetic and non planar ?



EXERCISE # S-1

INTEGER TYPE

- Find number of ligands which is / are stronger ligand as compared to NH_3
 NO_2^- , H_2O , NO_3^- , F^- , $\text{C}_2\text{O}_4^{2-}$, en, Cl^- , CN^-
- If crystal field stabilization energy of $[\text{ML}_6]^{+n}$ is $-0.8 \Delta_O$.
 Find minimum number of electrons in t_{2g} orbitals of metal ion ?
- Find number of Co–N linkage in,
Pentaamminecobalt(III)– μ –amidodiamminetriaquacobalt(III) chloride.
- Find the EAN value of central atom of $[\text{Fe}(\pi\text{-C}_4\text{H}_4)(\text{CO})_3]$
- Find the maximum number of atoms lying in one plane for $[\text{Cr}(\text{CN})_6]^{3-}$
- Select complex in which metal–carbon linkage(s) is / are present :
 $[\text{Fe}^{\text{III}}(\text{EDTA})]^-$, $\text{K}[\text{PtCl}_3(\pi\text{-C}_2\text{H}_4)]$, $[\text{Cr}(\text{acac})_3]^0$, $[\text{Fe}(\text{CO})_5]$, $[\text{Co}(\text{C}_2\text{H}_5\text{O})_6]^{3-}$, $[\text{Ni}(\text{dmg})_2]$
- Find out the total number of geometrical isomers of $[\text{Co}(\text{H}_2\text{O})_3\text{Cl}_3]$.
- Find the value of E.A.N of $[\text{Pd}(\text{CO})_4]^{+2}$ (atomic number = 46) :
- A co-ordination compound have magnetic moment 5.92 B.M. Find out the number of unpaired electron(s) in the compound.
- Find the number of optically active isomers for $[\text{Pd}(\text{en})_2(\text{NH}_3)(\text{H}_2\text{O})]^{4+}$ cation.

EXERCISE # S-2

MATCH THE COLUMN :

1. Match the complexes in column-I with the EAN of central atom in column-II:

Column-I	Column-II
(A) $[\text{Fe}(\text{CO})_4]^{2-}$	(P) 34
(B) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	(Q) 35
(C) $\text{K}_2[\text{Ni}(\text{CN})_4]$	(R) 36
(D) $[\text{Cu}(\text{NH}_3)_4]^{2+}$	(S) 37

2. **Column - I** **Column -II**

(A) $\text{Na}_2 [\text{Fe}(\text{CN})_5 \text{NO}]$	(P) $\mu = 0 \text{ B.M.}$
(B) $[\text{Fe}(\text{H}_2\text{O})_5 \text{NO}] \text{SO}_4$	(Q) octahedral
(C) $[\text{Ag}(\text{CN})_2]^-$	(R) $\mu = \sqrt{15} \text{ B.M.}$
(D) $\text{K}_4[\text{Fe}(\text{CN})_6]$	(S) NO^+ ligand

3. Match the complexes in column I with their stereoproperties in column II

Column I	Column II
(A) $[\text{CoCl}_3(\text{NH}_3)_3]$	(P) Has a facial isomer
(B) $[\text{Cr}(\text{ox})_3]^{3-}$	(Q) Cis form is optically active
(C) $[\text{CrCl}_2(\text{ox})_2]$	(R) Trans form is optically inactive
(D) $[\text{RhCl}_3(\text{Py})_3]$	(S) Has a meridional form
	(T) Two optically active isomer

4. Match each coordination compound in List-I with co-ordination number of central metal/ion from List-II and select the correct answer using the code given below the lists.

List-I	List-II
(P) $[\text{Co}(\text{en})_3]^{3+}$	(1) 6
(Q) $[\text{Ca}(\text{EDTA})]^{2-}$	(2) 4
(R) $[\text{Ni}(\text{CO})_4]$	(3) 2
(S) $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$	(4) 5

Code :

	P	Q	R	S
(A)	2	1	2	3
(B)	1	1	2	3
(C)	1	4	2	3
(D)	1	1	3	2

5. Match the List-I with List-II :

List-I

- (P) Ferrocene
(Q) $\text{Mn}_2(\text{CO})_{10}$
(R) Vitamine B_{12}
(S) Haemoglobin

List-II

- (1) Iron present
(2) Cobalt
(3) Metal-Metal bonding
(4) Sandwich structure

Code :

	P	Q	R	S
(A)	4	3	1	2
(B)	1	3	1	2
(C)	1,4	3	2	1
(D)	1	3	4	2

6. Match the List-I with List-II :

List-I

- (P) EDTA^{4-}
(Q) en
(R) gly^-
(S) amide

List-II

- (1) N-donor atom
(2) Chelate ligand with same donor site
(3) Bidentate with different donor atom
(4) Hexadentate

Code :

	P	Q	R	S
(A)	4	2	1	3
(B)	2	1	3	4
(C)	4	1	2	3
(D)	4	2	3	1

Assertion Reason :

7. **Statement-1:** Complexes containing three bidentate groups such as $[\text{Cr}(\text{ox})_3]^{3-}$ and $[\text{Co}(\text{en})_3]^{3+}$ do not show optical activity.

Statement-2: Octahedral complex, $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ shows geometrical isomerism.

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
(C) Statement-1 is true, statement-2 is false.
(D) Statement-1 is false, statement-2 is true.

8. **Statement-1:** After splitting of d-orbitals during complex formation, the orbitals form two sets of orbitals t_{2g} and e_g in an octahedral field.

Statement-2: Splitting of d-orbitals occur only in the case of strong field ligands such as CN^- .

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
(C) Statement-1 is true, statement-2 is false.
(D) Statement-1 is false, statement-2 is true.

9. **Statement-1:** $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ is coloured while $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$ is colourless.
Statement-2: d-d transition is not possible in $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$ because no d-electron is present while possible for Ti^{3+} having d^1 system.
- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
 (C) Statement-1 is true, statement-2 is false.
 (D) Statement-1 is false, statement-2 is true.

Comprehension (10 to 12)

Ligands are neutral or ionic species capable of donating at least one electron pair to central metal. Hence ligands can be of different denticities.

10. For a given metal M^{3+} coordination number is six, then for which set of ligands, complex will be most stable-
- (A) $6\text{H}_2\text{O}$ (B) 6F^- (C) EDTA^{4-} (D) $2\text{H}_2\text{O}$ and $2\text{C}_2\text{O}_4^{2-}$
11. $[\text{Mn}(\text{CO})_5]$ can attain more stability by :
- (A) Oxidation of itself (B) Reduction of itself
 (C) Dimerization (D) Both (B) and (C)
12. The metal cation that has least tendency to accept electron pair from NH_3 is
- (A) Fe^{3+} (B) Rh^{3+} (C) Zn^{2+} (D) Ba^{++}

Comprehension (13 to 15)

Complex compounds are molecular compounds which retain their identities even when dissolved in water. They do not give all the simple ions in solution but instead furnish complex ions with complicated structures. The complex compounds are often called coordination compounds because certain groups called ligands are attached to the central metal ion by coordinate or dative bonds. Coordination compounds exhibit isomerism, both structural and stereoisomerism. The structure, magnetic property, colour and electrical properties of complexes are explained by various theories.

13. Arrange the following compounds in order of their Molar conductance:
- (I) $\text{K}[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]$ (II) $[\text{Cr}(\text{ONO})_3(\text{NH}_3)_3]$
 (III) $[\text{Cr}(\text{NO}_2)(\text{NH}_3)_5]_3[\text{Co}(\text{NO}_2)_6]_2$ (IV) $\text{Mg}[\text{Cr}(\text{NO}_2)_5(\text{NH}_3)]$
 (A) $\text{II} < \text{I} < \text{IV} < \text{III}$ (B) $\text{I} < \text{II} < \text{III} < \text{IV}$
 (C) $\text{II} < \text{I} < \text{III} < \text{IV}$ (D) $\text{IV} < \text{III} < \text{II} < \text{I}$
14. The oxidation number and coordination number of chromium in the following complex is $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{NH}_3)_2]^{1-}$
- (A) O.N. = +4, C.N. = 4 (B) O.N. = +3, C.N. = 4
 (C) O.N. = -1, C.N. = 4 (D) O.N. = +3, C.N. = 6
15. In which of the following pairs, both the complexes have the same geometry but different hybridisation
- (A) $[\text{NiCl}_4]^{2-}$, $[\text{Ni}(\text{CN})_4]^{2-}$ (B) $[\text{CoF}_6]^{3-}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$
 (C) $[\text{Ni}(\text{CO})_4]$, $[\text{Ni}(\text{CN})_4]^{2-}$ (D) $[\text{Cu}(\text{NH}_3)_4]^{2+}$, $[\text{Ni}(\text{NH}_3)_6]^{2+}$

Matching list type 1 × 3Q. (Three list type Question)

The following column I, II, III represent the different type of observations based on CFT in complex compounds.

Answer the questions that follow

Column-I - Crystal field stabilization energy (CFSE) (neglecting PE in all cases)

Column-II - Electronic configuration

Column-III - Type of complex

Column - I CFSE (neglecting PE in all cases)	Column - II Electronic Configuration	Column - III Type of Complex
(I) $-0.4 \Delta_o$	(i) t_{2g}^5, e_g^0	(P) High spin & Paramagnetic
(II) $-2.0 \Delta_o$	(ii) t_{2g}^4, e_g^0	(Q) Low spin & Paramagnetic
(III) $-2.4 \Delta_o$	(iii) t_{2g}^6, e_g^0	(R) High spin & Diamagnetic
(IV) $-1.2 \Delta_o$	(iv) t_{2g}^4, e_g^2	(S) Low spin & Diamagnetic

16. For sodium nitroprusside complex the only **CORRECT** combination is
 (A) (III), (iv), (Q) (B) (III), (iii), (S) (C) (III), (iii), (R) (D) (II), (iii), (Q)
17. For $[\text{Co}(\text{H}_2\text{O})_3\text{F}_3]$ complex the only **CORRECT** combination is.
 (A) (I), (iv), (Q) (B) (II), (iv), (S) (C) (III), (ii), (R) (D) (I), (iv), (P)
18. For $[\text{Mn}(\text{CN})_6]^{4-}$ complex the only **CORRECT** combination is.
 (A) (IV), (i), (S) (B) (II), (i), (R) (C) (I), (i), (S) (D) (II), (i), (Q)

EXERCISE # JEE-MAIN

- In $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$, the isomerism shown is - [AIEEE-2002]
 (1) Ligand (2) Optical (3) Geometrical (4) Ionization
- In the complexes $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Fe}(\text{SCN})_6]^{3-}$, $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ and $[\text{FeCl}_6]^{3-}$, more stability is shown by - [AIEEE-2002]
 (1) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ (2) $[\text{Fe}(\text{SCN})_6]^{3-}$ (3) $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ (4) $[\text{FeCl}_6]^{3-}$
- One mole of the complex compound $\text{Co}(\text{NH}_3)_5\text{Cl}_3$, gives 3 moles of ions on dissolution in water. One mole of the same complex reacts with two moles of AgNO_3 solution to yield two moles of $\text{AgCl}(\text{s})$. The structure of the complex is - [AIEEE-2003]
 (1) $[\text{Co}(\text{NH}_3)_3\text{Cl}_3] \cdot 2\text{NH}_3$ (2) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl} \cdot \text{NH}_3$
 (3) $[\text{Co}(\text{NH}_3)_4\text{Cl}]\text{Cl}_2 \cdot \text{NH}_3$ (4) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
- In the coordination compound $\text{K}_4[\text{Ni}(\text{CN})_4]$, the oxidation state of nickel is - [AIEEE-2003]
 (1) 0 (2) +1 (3) +2 (4) -1
- The number of 3d-electrons remained in Fe^{2+} (At.no. of Fe = 26) ion is - [AIEEE-2003]
 (1) 4 (2) 5 (3) 6 (4) 3
- Ammonia forms the complex ion $[\text{Cu}(\text{NH}_3)_4]^{2+}$ with copper ions in alkaline solutions but not in acidic solution. What is the reason for it :- [AIEEE-2003]
 (1) In acidic solutions hydration protects copper ions
 (2) In acidic solutions protons coordinate with ammonia molecules forming NH_4^+ ions and NH_3 molecules are not available
 (3) In alkaline solutions insoluble $\text{Cu}(\text{OH})_2$ is precipitated which is soluble in excess of any alkali
 (4) Copper hydroxide is an amphoteric substance
- Among the properties (a) reducing (b) oxidising (c) complexing, the set of properties shown by CN^- ion towards metal species is :- [AIEEE-2004]
 (1) c, a (2) b, c (3) a, b (4) a, b, c
- The coordination number of a central metal atom in a complex is determined by :- [AIEEE-2004]
 (1) The number of ligands around a metal ion bonded by sigma and pi-bonds both
 (2) The number of ligands around a metal ion bonded by pi-bonds
 (3) The number of ligands around a metal ion bonded by sigma bonds
 (4) The number of only anionic ligands bonded to the metal ion
- Which one of the following complexes is an outer orbital complex :- [AIEEE-2004]
 (1) $[\text{Co}(\text{NH}_3)_6]^{3+}$ (2) $[\text{Mn}(\text{CN})_6]^{4-}$
 (3) $[\text{Fe}(\text{CN})_6]^{4-}$ (4) $[\text{Ni}(\text{NH}_3)_6]^{2+}$
 (Atomic nos.: Mn=25 ; Fe=26 ; Co=27 ; Ni = 28)

10. Coordination compounds have great importance in biological systems. In this context which of the following statements is **INCORRECT** ? [AIEEE-2004]
- (1) Cyanocobalamin is vitamin B₁₂ and contains cobalt
 - (2) Haemoglobin is the red pigment of blood and contains iron
 - (3) Chlorophylls are green pigments in plants and contain calcium
 - (4) Carboxypeptidase - A is an enzyme and contains zinc
11. The **CORRECT** order of magnetic moments (spin only values in B.M.) among is :- [AIEEE-2004]
- (1) $[\text{Fe}(\text{CN})_6]^{4-} > [\text{MnCl}_4]^{2-} > [\text{CoCl}_4]^{2-}$
 - (2) $[\text{MnCl}_4]^{2-} > [\text{Fe}(\text{CN})_6]^{4-} > [\text{CoCl}_4]^{2-}$
 - (3) $[\text{MnCl}_4]^{2-} > [\text{CoCl}_4]^{2-} > [\text{Fe}(\text{CN})_6]^{4-}$
 - (4) $[\text{Fe}(\text{CN})_6]^{4-} > [\text{CoCl}_4]^{2-} > [\text{MnCl}_4]^{2-}$
- (Atomic nos. : Mn = 25, Fe = 26, Co = 27)
12. For octahedral complex, the value of the 'spin only' magnetic moment for one of the following configurations is 2.84 BM. The **CORRECT** one is [AIEEE-2005]
- (1) d⁴ (in strong ligand field)
 - (2) d⁴ (in weak ligand field)
 - (3) d³ (in weak as well as in strong field)
 - (4) d⁵ (in strong ligand field)
13. The IUPAC name for the complex $[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]\text{Cl}_2$ is - [AIEEE-2006]
- (1) pentaammine nitrito-N- cobalt (II) chloride
 - (2) pentaammine nitrito-N- cobalt (III) chloride
 - (3) nitrito-N- pentaamminecobalt (III) chloride
 - (4) nitrito-N- pentaamminecobalt (II) chloride
14. Nickel (Z=28) combines with a uninegative monodentate ligand X⁻ to form a paramagnetic complex $[\text{NiX}_4]^{2-}$. The number of unpaired electrons in the nickel and geometry of this complex ion are, respectively. [AIEEE-2006]
- (1) one, square planar
 - (2) two, square planar
 - (3) one, tetrahedral
 - (4) two, tetrahedral
15. In $\text{Fe}(\text{CO})_5$, the Fe-C bond possesses [AIEEE-2006]
- (1) ionic character
 - (2) σ - character only
 - (3) π -character only
 - (4) both σ and π character
16. How many EDTA (ethylenediaminetetraacetate) molecules are required to make an octahedral complex with a Ca²⁺ ion ? [AIEEE-2006]
- (1) One
 - (2) Two
 - (3) Six
 - (4) Three
17. The "spin-only" magnetic moment [in units of Bohr magneton, (μ_B)] of Ni²⁺ in aqueous solution would be (At. No. Ni= 28)- [AIEEE-2006]
- (1) 0
 - (2) 1.73
 - (3) 2.84
 - (4) 4.90

18. Which one of the following has a square planar geometry :-
(Co = 27, Ni = 28, Fe = 26, Pt = 78) [AIEEE-2007]
(1) $[\text{CoCl}_4]^{2-}$ (2) $[\text{FeCl}_4]^{2-}$ (3) $[\text{NiCl}_4]^{2-}$ (4) $[\text{PtCl}_4]^{2-}$
19. The coordination number and the oxidation state of the element 'E' in the complex $[\text{E}(\text{en})_2(\text{C}_2\text{O}_4^{2-})]\text{NO}_2^0$ (where en) is ethylene diamine) are, respectively - [AIEEE-2008]
(1) 6 and 2 (2) 4 and 2 (3) 4 and 3 (4) 6 and 3
20. In which of the following octahedral complexes of Co (at. no. 27), will the magnitude of Δ_0 be the highest ? [AIEEE-2008]
(1) $[\text{Co}(\text{CN})_6]^{3-}$ (2) $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$ (3) $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ (4) $[\text{Co}(\text{NH}_3)_6]^{3+}$
21. Which of the following pairs represent linkage isomers ? [AIEEE-2009]
(1) $[\text{Co}(\text{NH}_3)_5\text{NO}_3]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{NO}_3$
(2) $[\text{PtCl}_2(\text{NH}_3)_4]\text{Br}_2$ and $[\text{PtBr}_2(\text{NH}_3)_4]\text{Cl}_2$
(3) $[\text{Cu}(\text{NH}_3)_4][\text{PtCl}_4]$ and $[\text{Pt}(\text{NH}_3)_4][\text{CuCl}_4]$
(4) $[\text{Pd}(\text{PPh}_3)_2(\text{NCS})_2]$ and $[\text{Pd}(\text{PPh}_3)_2(\text{SCN})_2]$
22. Which of the following has an optical isomer? [AIEEE-2009]
(1) $[\text{Co}(\text{H}_2\text{O})_4(\text{en})]^{3+}$ (2) $[\text{Co}(\text{en})_2(\text{NH}_3)_2]^{3+}$
(3) $[\text{Co}(\text{NH}_3)_3\text{Cl}]^+$ (4) $[\text{Co}(\text{en})(\text{NH}_3)_2]^{2+}$
23. Which one of the following has an optical isomer ? [AIEEE-2010]
(1) $[\text{Zn}(\text{en})_2]^{2+}$ (2) $[\text{Zn}(\text{en})(\text{NH}_3)_2]^{2+}$ (3) $[\text{Co}(\text{en})_3]^{3+}$ (4) $[\text{Co}(\text{H}_2\text{O})_4(\text{en})]^{3+}$
(en = ethylenediamine)
24. A solution containing 2.675 g of $\text{CoCl}_3 \cdot 6\text{NH}_3$ (molar mass = 267.5 g mol^{-1}) is passed through a cation exchanger. The chloride ions obtained in solution were treated with excess of AgNO_3 to give 4.78 g of AgCl (molar mass = 143.5 g mol^{-1}). The formula of the complex is :- [AIEEE-2010]
(At. mass of Ag = 108 u)
(1) $[\text{CoCl}(\text{NH}_3)_5]\text{Cl}_2$ (2) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ (3) $[\text{CoCl}_2(\text{NH}_3)_4]\text{Cl}$ (4) $[\text{CoCl}_3(\text{NH}_3)_3]$
25. Which of the following facts about the complex $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$ is **wrong** ? [AIEEE-2011]
(1) The complex is an outer orbital complex
(2) The complex gives white precipitate with silver nitrate solution
(3) The complex involves d^2sp^3 hybridisation and is octahedral in shape
(4) The complex is paramagnetic
26. The magnetic moment (spin only) of $[\text{NiCl}_4]^{2-}$ is :- [AIEEE-2011]
(1) 2.82 BM (2) 1.41 BM (3) 1.82 BM (4) 5.46 BM
27. Among the ligands NH_3 , en, CN^- and CO the **CORRECT** order of their increasing field strength, is :- [AIEEE-2011]
(1) $\text{CO} < \text{NH}_3 < \text{en} < \text{CN}^-$ (2) $\text{NH}_3 < \text{en} < \text{CN}^- < \text{CO}$
(3) $\text{CN}^- < \text{NH}_3 < \text{CO} < \text{en}$ (4) $\text{en} < \text{CN}^- < \text{NH}_3 < \text{CO}$
28. Which one of the following complex ions has geometrical isomers ? [AIEEE-2011]
(1) $[\text{Co}(\text{en})_3]^{3+}$ (2) $[\text{Ni}(\text{NH}_3)_5\text{Br}]^+$
(3) $[\text{Co}(\text{NH}_3)_2(\text{en})_2]^{3+}$ (4) $[\text{Cr}(\text{NH}_3)_4(\text{en})]^{3+}$
29. Which among the following will be named as dibromidobis (ethylene diamine) chromium (III) bromide ? [AIEEE-2012]
(1) $[\text{Cr}(\text{en})\text{Br}_2]\text{Br}$ (2) $[\text{Cr}(\text{en})_3]\text{Br}_3$ (3) $[\text{Cr}(\text{en})_2\text{Br}_2]\text{Br}$ (4) $[\text{Cr}(\text{en})\text{Br}_4]^-$

30. The complex ion $[\text{Pt}(\text{NO}_2)(\text{Py})(\text{NH}_3)(\text{NH}_2\text{OH})]^+$ will give :- [J-MAIN-2012, Online]
 (1) 4 isomers (Geometrical) (2) 2 isomers (Geometrical)
 (3) 3 isomers (Geometrical) (4) 6 isomers (Geometrical)
31. Which of the following complex ions will exhibit optical isomerism? [J-MAIN-2012, Online]
 (en = 1, 2-diamine ethane)
 (1) $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ (2) $[\text{Zn}(\text{en})_2]^{2+}$
 (3) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ (4) $[\text{Cr}(\text{NH}_3)_2\text{Cl}_2]^+$
32. Which of the following complex species is **NOT** expected to exhibit optical isomerism ? [J-MAIN-2013]
 (1) $[\text{Co}(\text{en})_3]^{3+}$ (2) $[\text{Co}(\text{en})_2\text{Cl}_2]^+$
 (3) $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ (4) $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]^+$
33. Type of isomerism which exists between $[\text{Pd}(\text{C}_6\text{H}_5)_2(\text{SCN})_2]$ and $[\text{Pd}(\text{C}_6\text{H}_5)_2(\text{NCS})_2]$ is : [J-MAIN-2013, Online]
 (1) Solvate isomerism (2) Ionisation isomerism
 (3) Linkage isomerism (4) Coordination isomerism
34. Which of the following is diamagnetic ? [J-MAIN-2013, Online]
 (1) $[\text{CoF}_6]^{3-}$ (2) $[\text{FeF}_6]^{3-}$ (3) $[\text{Fe}(\text{CN})_6]^{3-}$ (4) $[\text{Co}(\text{Ox})_3]^{3-}$
35. The magnetic moment of the complex anion $[\text{Cr}(\text{NO})(\text{NH}_3)(\text{CN})_4]^{2-}$ is : [J-MAIN-2013, Online]
 (1) 2.82 BM (2) 5.91 BM (3) 1.73 BM (4) 3.87 BM
36. The octahedral complex of a metal ion M^{3+} with four monodentate ligands L_1 , L_2 , L_3 and L_4 absorb wavelength in the region of red, green, yellow and blue, respectively. The increasing order of ligand strength of the four ligands is: [J-MAIN-2014]
 (1) $\text{L}_3 < \text{L}_2 < \text{L}_4 < \text{L}_1$ (2) $\text{L}_1 < \text{L}_2 < \text{L}_4 < \text{L}_3$
 (3) $\text{L}_4 < \text{L}_3 < \text{L}_2 < \text{L}_1$ (4) $\text{L}_1 < \text{L}_3 < \text{L}_2 < \text{L}_4$
37. The equation which is balanced and represents the **CORRECT** product (s) is : [J-MAIN-2014]
 (1) $[\text{Mg}(\text{H}_2\text{O})_6]^{2+} + (\text{EDTA})^{4-} \xrightarrow{\text{excess NaOH}} [\text{Mg}(\text{EDTA})]^{2-} + 6\text{H}_2\text{O}$
 (2) $\text{CuSO}_4 + 4\text{KCN} \rightarrow \text{K}_2[\text{Cu}(\text{CN})_4] + \text{K}_2\text{SO}_4$
 (3) $\text{Li}_2\text{O} + 2\text{KCl} \rightarrow 2\text{LiCl} + \text{K}_2\text{O}$
 (4) $[\text{CoCl}(\text{NH}_3)_5]^+ + 5\text{H}^+ \rightarrow \text{Co}^{2+} + 5\text{NH}_4^+ + \text{Cl}^-$
38. The **CORRECT** statement about the magnetic properties of $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{FeF}_6]^{3-}$ is : (Z = 26). [J-MAIN-2014, Online]
 (1) $[\text{Fe}(\text{CN})_6]^{3-}$ is paramagnetic, $[\text{FeF}_6]^{3-}$ is diamagnetic.
 (2) both are diamagnetic.
 (3) $[\text{Fe}(\text{CN})_6]^{3-}$ is diamagnetic, $[\text{FeF}_6]^{3-}$ is paramagnetic.
 (4) both are paramagnetic
39. An octahedral complex of Co^{3+} is diamagnetic. The hybridisation involved in the formation of the complex is : [J-MAIN-2014]
 (1) d^2sp^3 (2) dsp^3d (3) dsp^2 (4) sp^3d^2

40. Which of the following name formula combinations is **NOT CORRECT**? [J-MAIN-2014, Online]

Formula

Name

- | | |
|-------------------------------|--|
| (1) $K[Cr(NH_3)_2Cl_4]$ | Potassium diammine Tetrachlorochromate (III) |
| (2) $[Co(NH_3)_4(H_2O)I]SO_4$ | Tetraammine aquaiodo cobalt (III) sulphate |
| (3) $[Mn(CN)_5]^{2-}$ | Pentacyanomagnate (II) ion |
| (4) $K_2[Pt(CN)_4]$ | Potassium tetracyanoplatinate(II) |

41. Consider the coordination compound, $[Co(NH_3)_6]Cl_3$. In the formation of this complex, the species which acts as the Lewis acid is : [J-MAIN-2014, Online]

- (1) $[Co(NH_3)_6]^{3+}$ (2) NH_3 (3) Co^{3+} (4) Cl^-

42. Among the following species the one which causes the highest CFSE, Δ_0 as a ligand is :- [J-MAIN-2014, Online]

- (1) CN^- (2) NH_3 (3) CO (4) F^-

43. Which one of the following complexes will most likely absorb visible light ? [J-MAIN-2014, Online] (At nos. Sc = 21, Ti = 22, V = 23, Zn = 30) :-

- (1) $[Ti(NH_3)_6]^{4+}$ (2) $[V(NH_3)_6]^{3+}$ (3) $[Zn(NH_3)_6]^{2+}$ (4) $[Sc(H_2O)_6]^{3+}$

44. Nickel (Z = 28) combines with a uninegative monodentate ligand to form a diamagnetic complex $[NiL_4]^{2-}$. The hybridisation involved and the number of unpaired electrons present in the complex are respectively : [J-MAIN-2014, Online]

- (1) sp^3 , zero (2) sp^3 , two (3) dsp^2 , one (4) dsp^2 , zero

45. The number of geometrical isomers that can exist for square planar $[Pt(Cl)(py)(NH_3)(NH_2OH)]^+$ is (py = pyridine) : [J-MAIN-2015]

- (1) 4 (2) 6 (3) 2 (4) 3

46. The color of $KMnO_4$ is due to : [J-MAIN-2015]

- (1) $L \rightarrow M$ charge transfer transition (2) $\sigma - \sigma^*$ transition
(3) $M \rightarrow L$ charge transfer transition (4) $d - d$ transition

47. Which of the following complex ions has electrons that are symmetrically filled in both t_{2g} and e_g orbitals ? [J-MAIN-2015, Online]

- (1) $[CoF_6]^{3-}$ (2) $[Mn(CN)_6]^{4-}$ (3) $[FeF_6]^{3-}$ (4) $[Co(NH_3)_6]^{2+}$

48. When concentrated HCl is added to an aqueous solution of $CoCl_2$, its colour changes from reddish pink to deep blue. Which complex ion gives blue colour in this reaction ?:- [J-MAIN-2015, Online]

- (1) $[Co(H_2O)_6]^{2+}$ (2) $[CoCl_6]^{3-}$
(3) $[CoCl_4]^{2-}$ (4) $[CoCl_6]^{4-}$

49. The **CORRECT** statement on the isomerism associated with the following complex ions, [J-MAIN-2015, Online]

- (a) $[Ni(H_2O)_5NH_3]^{2+}$
(b) $[Ni(H_2O)_4(NH_3)_2]^{2+}$ and
(c) $[Ni(H_2O)_3(NH_3)_3]^{2+}$ is :

- (1) (a) and (b) show geometrical and optical isomerism
(2) (b) and (c) show geometrical and optical isomerism
(3) (a) and (b) show only geometrical Isomerism
(4) (b) and (c) show only geometrical Isomerism

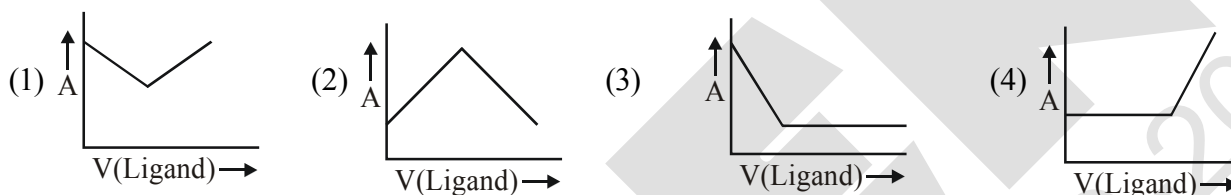
50. Which one of the following complexes shows optical isomerism :- [J-MAIN-2016]
 (1) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ (2) $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$
 (3) $\text{cis}[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ (4) $\text{trans}[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$
 (en = ethylenediamine)
51. The pair having the same magnetic moment is:- [J-MAIN-2016]
 [At. No.: Cr = 24, Mn = 25, Fe = 26, Co = 27]
 (1) $[\text{CoCl}_4]^{2-}$ and $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ (2) $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{CoCl}_4]^{2-}$
 (3) $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ (4) $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$
52. Which one of the following complexes will consume more equivalents of aqueous solution of $\text{Ag}(\text{NO}_3)$? [J-MAIN-2016, Online]
 (1) $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ (2) $\text{Na}_2[\text{CrCl}_5(\text{H}_2\text{O})]$ (3) $\text{Na}_3[\text{CrCl}_6]$ (4) $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2$
53. Identify the **CORRECT** trend given below : [J-MAIN-2016, Online]
 (Atomic No. = Ti : 22, Cr : 24 and Mo : 42)
 (1) Δ_0 of $[\text{Cr}(\text{H}_2\text{O})_6]^{2+} < [\text{Mo}(\text{H}_2\text{O})_6]^{2+}$ and Δ_0 of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+} < [\text{Ti}(\text{H}_2\text{O})_6]^{2+}$
 (2) Δ_0 of $[\text{Cr}(\text{H}_2\text{O})_6]^{2+} < [\text{Mo}(\text{H}_2\text{O})_6]^{2+}$ and Δ_0 of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+} > [\text{Ti}(\text{H}_2\text{O})_6]^{2+}$
 (3) Δ_0 of $[\text{Cr}(\text{H}_2\text{O})_6]^{2+} > [\text{Mo}(\text{H}_2\text{O})_6]^{2+}$ and Δ_0 of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+} > [\text{Ti}(\text{H}_2\text{O})_6]^{2+}$
 (4) Δ_0 of $[\text{Cr}(\text{H}_2\text{O})_6]^{2+} > [\text{Mo}(\text{H}_2\text{O})_6]^{2+}$ and Δ_0 of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+} < [\text{Ti}(\text{H}_2\text{O})_6]^{2+}$
54. $[\text{Co}_2(\text{CO})_8]$ displays:- [J-MAIN-2017, Online]
 (1) no Co-Co bond, four terminal CO and four bridging CO
 (2) one Co-Co bond, six terminal CO and two bridging CO
 (3) no Co-Co bond, six terminal CO and two bridging CO
 (4) one Co-Co bond, four terminal CO and four bridging CO
55. On treatment of 100 mL of 0.1 M solution of $\text{CoCl}_3 \cdot 6\text{H}_2\text{O}$ with excess AgNO_3 ; 1.2×10^{22} ions are precipitated. The complex is :- [J-MAIN-2017, Offline]
 (1) $[\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ (2) $[\text{Co}(\text{H}_2\text{O})_3\text{Cl}_3] \cdot 3\text{H}_2\text{O}$
 (3) $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_3$ (4) $[\text{Co}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$
56. The pair of compounds having metal in their highest oxidation state is : [J-MAIN-2017, Online]
 (1) $[\text{NiCl}_4]^{2-}$ and $[\text{CoCl}_4]^{2-}$ (2) $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Cu}(\text{CN})_4]^{2-}$
 (3) $[\text{FeCl}_4]^-$ and Co_2O_3 (4) MnO_2 and CrO_2Cl_2
57. The oxidation states of Cr in $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$, $[\text{Cr}(\text{C}_6\text{H}_6)_2]$, and $\text{K}_2[\text{Cr}(\text{CN})_2(\text{O})_2(\text{O}_2)(\text{NH}_3)]$ respectively are : [J-MAIN-2018, Offline]
 (1) +3, +2, and +4 (2) +3, 0, and +6
 (3) +3, 0, and +4 (4) +3, +4, and +6

58. Consider the following reaction and statements : [J-MAIN-2018, Offline]
 $[\text{Co}(\text{NH}_3)_4\text{Br}_2]^+ + \text{Br}^- \rightarrow [\text{Co}(\text{NH}_3)_3\text{Br}_3] + \text{NH}_3$
 (I) Two isomers are produced if the reactant complex ion is a *cis*-isomer.
 (II) Two isomers are produced if the reactant complex ion is a *trans*-isomer.
 (III) Only one isomer is produced if the reactant complex ion is a *trans*-isomer.
 (IV) Only one isomer is produced if the reactant complex ion is a *cis*-isomer.
 The correct statements are :
 (1) (I) and (III) (2) (III) and (IV) (3) (II) and (IV) (4) (I) and (II)
59. For 1 molal aqueous solution of the following compounds, which one will show the highest freezing point ? [J-MAIN-2018, Offline]
 (1) $[\text{Co}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$
 (2) $[\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$
 (3) $[\text{Co}(\text{H}_2\text{O})_3\text{Cl}_3] \cdot 3\text{H}_2\text{O}$
 (4) $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_3$
60. The total number of possible isomers for square-planar $[\text{Pt}(\text{Cl})(\text{NO}_2)(\text{NO}_3)(\text{SCN})]^{2-}$ is :- [J-MAIN-2018, Online]
 (1) 16 (2) 8 (3) 24 (4) 12
61. The correct order of spin-only magnetic moments among the following is : [J-MAIN-2018, Online]
 (Atomic number : Mn = 25, Co = 27, Ni = 28, Zn = 30)
 (1) $[\text{ZnCl}_4]^{2-} > [\text{NiCl}_4]^{2-} > [\text{CoCl}_4]^{2-} > [\text{MnCl}_4]^{2-}$
 (2) $[\text{CoCl}_4]^{2-} > [\text{MnCl}_4]^{2-} > [\text{NiCl}_4]^{2-} > [\text{ZnCl}_4]^{2-}$
 (3) $[\text{MnCl}_4]^{2-} > [\text{CoCl}_4]^{2-} > [\text{NiCl}_4]^{2-} > [\text{ZnCl}_4]^{2-}$
 (4) $[\text{NiCl}_4]^{2-} > [\text{CoCl}_4]^{2-} > [\text{MnCl}_4]^{2-} > [\text{ZnCl}_4]^{2-}$
62. The correct combination is [J-MAIN-2018, Online]
 (1) $[\text{Ni}(\text{CN})_4]^{2-}$ – tetrahedral;
 $[\text{Ni}(\text{CO})_4]$ – paramagnetic
 (2) $[\text{NiCl}_4]^{2-}$ – paramagnetic;
 $[\text{Ni}(\text{CO})_4]$ – tetrahedral
 (3) $[\text{NiCl}_4]^{2-}$ – diamagnetic;
 $[\text{Ni}(\text{CO})_4]$ – square-planar
 (4) $[\text{NiCl}_4]^{2-}$ – square-planar;
 $[\text{Ni}(\text{CN})_4]^{2-}$ – paramagnetic

63. Which of the following complexes will show geometrical isomerism ? [J-MAIN-2018, Online]

- (1) Potassium amminetrichloroplatinate(II)
- (2) Aquachlorobis (ethylenediamine) cobalt(II) chloride
- (3) Potassium tris(oxalato) chromate(III)
- (4) Pentaquachlorochromium(III) chloride

64. In a complexometric titration of metal ion with ligand $M(\text{Metal ion}) + L(\text{Ligand}) \rightarrow C(\text{Complex})$ end point is estimated spectrophotometrically (through light absorption). If 'M' and 'C' do not absorb light and only 'L' absorbs, then the titration plot between absorbed light (A) versus volume of ligand 'L' (v) would look like :- [J-MAIN-2018, Online]



65. In Wilkinson's catalyst, the hybridization of central metal ion and its shape are respectively

- (1) dsp^2 , square planar
- (2) sp^3d , trigonal bipyramidal
- (3) sp^3 , tetrahedral
- (4) d^2sp^3 , octahedral

[J-MAIN-2018, Online]

EXERCISE # JEE-ADVANCED

- The complex ion which has no 'd' electrons in the central metal atom is : [JEE 2001]
[At No. Cr = 24, Mn = 25, Fe = 26, Co = 27]
(A) $[\text{MnO}_4]^-$ (B) $[\text{Co}(\text{NH}_3)_6]^{3+}$ (C) $[\text{Fe}(\text{CN})_6]^{3-}$ (D) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$
- The **CORRECT** order of hybridisation of the central atom in the following species. [JEE 2001]
 NH_3 , $[\text{PtCl}_4]^{2-}$, PCl_5 and BCl_3 is [At No. Pt = 78]
(A) $\text{dsp}^2, \text{sp}^3\text{d}, \text{sp}^2$ and sp^3 (B) $\text{sp}^3, \text{dsp}^2, \text{sp}^3\text{d}$, sp^2
(C) $\text{dsp}^2, \text{sp}^2, \text{sp}^3$ and sp^3d (D) dsp^2 , sp^3, sp^2 and sp^3d
- The species having tetrahedral shape is : [JEE 2004]
(A) $[\text{PdCl}_4]^{2-}$ (B) $[\text{Ni}(\text{CN})_4]^{2-}$ (C) $[\text{Pd}(\text{CN})_4]^{2-}$ (D) $[\text{NiCl}_4]^{2-}$
- The pair of compounds having metals in their highest oxidation state is [JEE 2004]
(A) MnO_2 , FeCl_3 (B) $[\text{MnO}_4]^-$, CrO_2Cl_2
(C) $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Co}(\text{CN})_3]$ (D) $[\text{NiCl}_4]^{2-}$, $[\text{CoCl}_4]^-$
- Spin only magnetic moment of the compound $\text{Hg}[\text{Co}(\text{SCN})_4]$ is [JEE 2004]
(A) $\sqrt{3}$ (B) $\sqrt{15}$ (C) $\sqrt{24}$ (D) $\sqrt{8}$
- Which of the following pair is expected to exhibit same colour in solution? [JEE 2005]
(A) VOCl_2 ; FeCl_2 (B) CuCl_2 ; VOCl_2 (C) MnCl_2 ; FeCl_2 (D) FeCl_2 ; CuCl_2
- Which type of isomerism is shown by $\text{Co}(\text{NH}_3)_4\text{Br}_2\text{Cl}$? [JEE 2005]
(A) Geometrical and Ionisation (B) Optical and Ionisation
(C) Geometrical and Optical (D) Geometrical only

Question No. 8 to 10 (3 questions)

[JEE 2006]

The coordination number of Ni^{2+} is 4. $\text{NiCl}_2 + \text{KCN} (\text{excess}) \rightarrow \text{A} (\text{cyano complex})$ $\text{NiCl}_2 + \text{KCl} (\text{excess}) \rightarrow \text{B} (\text{chloro complex})$

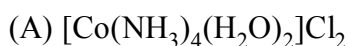
- The IUPAC name of A and B are
(A) Potassium tetracyanonickelate (II), potassium tetrachloridonickelate (II)
(B) Tetracyanidopotassiumnickelate (II), tetrachloridopotassiumnickelate (II)
(C) Tetracyanidonickel (II), tetrachloridonickel (II)
(D) Potassium tetracyanonickel (II), potassium tetrachloridonickel (II)
- Predict the magnetic nature of A and B.
(A) Both are diamagnetic.
(B) A is diamagnetic and B is paramagnetic with one unpaired electron.
(C) A is diamagnetic and B is paramagnetic with two unpaired electrons.
(D) Both are paramagnetic.
- The hybridization of A and B are
(A) dsp^2 , sp^3 (B) sp^3 , sp^3 (C) dsp^2 , dsp^2 (D) sp^3d^2 , d^2sp^3

11. If the bond length of CO bond in carbon monoxide is 1.128\AA , then what is the value of CO bond length in $\text{Fe}(\text{CO})_5$? [JEE 2006]
 (A) 1.15\AA (B) 1.128\AA (C) 1.72\AA (D) 1.118\AA
12. Among the following metal carbonyls, the C–O bond order is lowest in [JEE 2007]
 (A) $[\text{Mn}(\text{CO})_6]^+$ (B) $[\text{Fe}(\text{CO})_5]$ (C) $[\text{Cr}(\text{CO})_6]$ (D) $[\text{V}(\text{CO})_6]^-$
13. Match the complexes in Column I with their properties listed in Column II. Indicate your answer by darkening the appropriate bubbles of the 4×4 matrix given in the ORS. [JEE 2007]

Column I

Column II

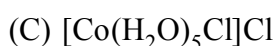
[JEE 2007]



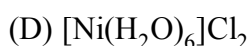
(P) Geometrical isomers



(Q) Paramagnetic



(R) Diamagnetic



(S) Metal ion with 2+ oxidation state

14. Among the following, the coloured compound is [JEE 2008]
 (A) CuCl (B) $\text{K}_3[\text{Cu}(\text{CN})_4]$ (C) CuF_2 (D) $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{BF}_4$

15. The IUPAC name of $[\text{Ni}(\text{NH}_3)_4][\text{NiCl}_4]$ is [JEE 2008]

- (A) Tetrachloronickel(II)-tetraamminenickel(II)
 (B) Tetraamminenickel(II)-tetrachloronickel(II)
 (C) Tetraamminenickel(II)-tetrachloronickelate(II)
 (D) Tetrachloronickel(II)-tetraamminenickelate(0)

16. Both $[\text{Ni}(\text{CO})_4]$ and $[\text{Ni}(\text{CN})_4]^{2-}$ are diamagnetic. The hybridisations of nickel in these complexes, respectively, are [JEE 2008]

- (A) sp^3, sp^3 (B) $\text{sp}^3, \text{dsp}^2$ (C) $\text{dsp}^2, \text{sp}^3$ (D) $\text{dsp}^2, \text{dsp}^2$

17. Statement-1 : The geometrical isomers of the complex $[\text{M}(\text{NH}_3)_4\text{Cl}_2]$ are optically inactive.
 Statement-2 : Both geometrical isomers of the complex $[\text{M}(\text{NH}_3)_4\text{Cl}_2]$ possess axis of symmetry.
 (A) Statement-1 is True, Statement-2 is True ; Statement-2 is a correct explanation for Statement-1
 (B) Statement-1 is True, Statement-2 is True ; Statement-2 is NOT a correct explanation for Statement-1
 (C) Statement-1 is True, Statement-2 is False
 (D) Statement-1 is False, Statement-2 is True [JEE 2008]

18. Statement-1 : $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$ is paramagnetic [JEE 2008]

Statement-2 : The Fe in $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$ has three unpaired electrons.

- (A) Statement-1 is True, Statement-2 is True ; Statement-2 is a correct explanation for Statement-1
 (B) Statement-1 is True, Statement-2 is True ; Statement-2 is NOT a correct explanation for Statement-1
 (C) Statement-1 is True, Statement-2 is False
 (D) Statement-1 is False, Statement-2 is True

19. The spin only magnetic moment value (in Bohr magneton units) of $\text{Cr}(\text{CO})_6$ is [JEE 2009]
 (A) 0 (B) 2.84 (C) 4.90 (D) 5.92

20. The compound(s) that exhibit(s) geometrical isomerism is (are) : [JEE 2009]
 (A) $[\text{Pt}(\text{en})\text{Cl}_2]$ (B) $[\text{Pt}(\text{en})_2]\text{Cl}_2$ (C) $[\text{Pt}(\text{en})_2\text{Cl}_2]\text{Cl}_2$ (D) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$
21. The number of water molecule(s) directly bonded to the metal centre in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is. [JEE 2009]
22. The ionization isomer of $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}(\text{NO}_2)]\text{Cl}$ is – [JEE 2010]
 (A) $[\text{Cr}(\text{H}_2\text{O})_4(\text{O}_2\text{N})]\text{Cl}_2$ (B) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2](\text{NO}_2)$
 (C) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}(\text{ONO})]\text{Cl}$ (D) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2(\text{NO}_2)] \cdot \text{H}_2\text{O}$
23. Total number of geometrical isomers for the complex $[\text{RhCl}(\text{CO})(\text{PPh}_3)(\text{NH}_3)]$ is. [JEE 2010]
24. The correct structure of ethylenediaminetetraacetic acid (EDTA) is – [JEE 2010]
 (A) $\begin{array}{c} \text{HOOC}-\text{CH}_2 \\ \text{HOOC}-\text{CH}_2 \end{array} \text{N}-\text{CH}=\text{CH}-\text{N} \begin{array}{c} \text{CH}_2-\text{COOH} \\ \text{CH}_2-\text{COOH} \end{array}$ (B) $\begin{array}{c} \text{HOOC} \\ \text{HOOC} \end{array} \text{N}-\text{CH}_2-\text{CH}_2-\text{N} \begin{array}{c} \text{COOH} \\ \text{COOH} \end{array}$
 (C) $\begin{array}{c} \text{HOOC}-\text{CH}_2 \\ \text{HOOC}-\text{CH}_2 \end{array} \text{N}-\text{CH}_2-\text{CH}_2-\text{N} \begin{array}{c} \text{CH}_2-\text{COOH} \\ \text{CH}_2-\text{COOH} \end{array}$ (D) $\begin{array}{c} \text{COOH} \\ \text{CH}_2 \\ \text{HOOC}-\text{CH}_2 \\ \text{H} \end{array} \text{N}-\text{CH}-\text{CH}-\text{N} \begin{array}{c} \text{H} \\ \text{CH}_2 \\ \text{CH}_2-\text{COOH} \\ \text{HOOC} \end{array}$
25. Geometrical shapes of the complexes formed by the reaction of Ni^{2+} with Cl^- , CN^- and H_2O respectively, are - [JEE 2011]
 (A) octahedral, tetrahedral and square planar (B) tetrahedral, square planar and octahedral
 (C) square planar, tetrahedral and octahedral (D) octahedral, square planar and octahedral
26. Among the following complexes (**K–P**) [JEE 2011]
 $\text{K}_3[\text{Fe}(\text{CN})_6]$ (**K**), $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ (**L**), $\text{Na}_3[\text{Co}(\text{oxalate})_3]$ (**M**), $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$ (**N**),
 $\text{K}_2[\text{Pt}(\text{CN})_4]$ (**O**) and $[\text{Zn}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ (**P**)
 The diamagnetic complex are -
 (A) K, L, M, N (B) K, M, O, P (C) L, M, O, P (D) L, M, N, O
27. The volume (in mL) of 0.1M AgNO_3 required for complete precipitation of chloride ions present in 30 mL of 0.01M solution of $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2$, as silver chloride is close to. [JEE 2011]
28. As per IUPAC nomenclature, the name of the complex $[\text{Co}(\text{H}_2\text{O})_4(\text{NH}_3)_2]\text{Cl}_3$ is : [JEE 2012]
 (A) Tetraaquadiamminecobalt(III) chloride (B) Tetraaquadiamminecobalt(III) chloride
 (C) Diaminetetraaquacobalt(III) chloride (D) Diamminetetraaquacobalt(III) chloride
29. The colour of light absorbed by an aqueous solution of CuSO_4 is - [JEE 2012]
 (A) orange-red (B) blue-green (C) yellow (D) violet
30. $\text{NiCl}_2 \cdot \text{P}(\text{C}_2\text{H}_5)_2(\text{C}_6\text{H}_5)_2$ exhibits temperature dependent magnetic behavior (paramagnetic/diamagnetic). The coordination geometries of Ni^{2+} in the paramagnetic and diamagnetic states are respectively : [JEE 2012]
 (A) tetrahedral and tetrahedral (B) square planar and square planar
 (C) tetrahedral and square planar (D) square planar and tetrahedral

31. Consider the following complex ions P, Q and R ,
 $P = [FeF_6]^{3-}$, $Q = [V(H_2O)_6]^{2+}$ and $R = [Fe(H_2O)_6]^{2+}$
 The **CORRECT** order of the complex ions, according to their spin-only magnetic moment values (in B.M.) is - **[JEE 2013]**
 (A) $R < Q < P$ (B) $Q < R < P$ (C) $R < P < Q$ (D) $Q < P < R$
32. $EDTA^{4-}$ is ethylenediaminetetraacetate ion. The total number of N–Co–O bond angles in $[Co(EDTA)]^{-1}$ complex ion is **[JEE 2013]**
33. The pair(s) of coordination complex/ion exhibiting the same kind of isomerism is(are) - **[JEE 2013]**
 (A) $[Cr(NH_3)_5Cl]Cl_2$ and $[Cr(NH_3)_4Cl_2]Cl$ (B) $[Co(NH_3)_4Cl_2]^+$ and $[Pt(NH_3)_2(H_2O)Cl]^+$
 (C) $[CoBr_2Cl_2]^{2-}$ and $[PtBr_2Cl_2]^{2-}$ (D) $[Pt(NH_3)_3(NO_3)]Cl$ and $[Pt(NH_3)_3Cl]Br$
34. Match each coordination compound in List-I with an appropriate pair of characteristics from List-II and select the correct answer using the code given below the lists. **[JEE Adv. 2014]**
 {en = $H_2NCH_2CH_2NH_2$ ' atomic numbers ; Ti = 22 ; Cr = 24 ; Co = 27 ; Pt = 78}

List-I

- (P) $[Cr(NH_3)_4Cl_2]Cl$
 (Q) $[Ti(H_2O)_5Cl](NO_3)_2$
 (R) $[Pt(en)(NH_3)Cl]NO_3$
 (S) $[Co(NH_3)_4(NO_3)_2]NO_3$

List-II

- (1) Paramagnetic and exhibits ionisation isomerism
 (2) Diamagnetic and exhibits *cis-trans* isomerism
 (3) Paramagnetic and exhibits *cis-trans* isomerism
 (4) Diamagnetic and exhibits ionisation isomerism

Code :

- | | P | Q | R | S |
|-----|---|---|---|---|
| (A) | 4 | 2 | 3 | 1 |
| (C) | 2 | 1 | 3 | 4 |

- | | P | Q | R | S |
|-----|---|---|---|---|
| (B) | 3 | 1 | 4 | 2 |
| (D) | 1 | 3 | 4 | 2 |

35. A list of species having the formula XZ_4 is given below : **[JEE Adv. 2014]**
 XeF_4 , SF_4 , SiF_4 , BF_4^- , BrF_4^- , $[Cu(NH_3)_4]^{2+}$, $[FeCl_4]^{2-}$, $[CoCl_4]^{2-}$ and $[PtCl_4]^{2-}$.
 Defining shape on the basis of the location of X and Z atoms, the total number of species having a square planar shape is

Subjective

36. Draw the structures of $[Co(NH_3)_6]^{3+}$, $[Ni(CN)_4]^{2-}$ and $[Ni(CO)_4]$. Write the hybridisation of atomic orbitals of the transition metal in each case. **[JEE 2000]**
37. A metal complex having composition $Cr(NH_3)_4Cl_2Br$ has been isolated in two forms A and B. The form A reacts with $AgNO_3$ to give a white precipitate readily soluble in dilute aqueous ammonia, whereas B gives a pale yellow precipitate soluble in concentrated ammonia. Write the formula of A and B and state the hybridisation of chromium in each. Calculate their magnetic moments (spin-only value). **[JEE 2001]**
38. Deduce the structures of $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ considering the hybridisation of the metal ion. Calculate the magnetic moment (spin only) of the species. **[JEE 2002]**

39. Write the IUPAC name of the compound $K_2[Cr(NO)(CN)_4(NH_3)]$. Spin magnetic moment of the complex $\mu = 1.73$ BM. Give the structure of anion. [JEE 2003]
40. $NiCl_2$ in the presence of dimethyl glyoxime (DMG) gives a complex which precipitates in the presence of NH_4OH , giving a bright red colour. [JEE 2004]
- (a) Draw its structure and show H-bonding
- (b) Give oxidation state of Ni and its hybridisation
- (c) Predict whether it is paramagnetic or diamagnetic
41. For the octahedral complexes of Fe^{3+} in SCN^- (thiocyanato-S) and in CN^- ligand environments, the difference between the spin only magnetic moments in Bohr magnetons (when approximated to the nearest integer) is : [Atomic number of Fe = 26] [JEE Ad. 2015]
42. In the complex acetylbromidodicarbonylbis(triethylphosphine)iron(II), the number of Fe–C bond(s) is- [JEE Ad. 2015]
43. Among the complex ions, $[Co(NH_2-CH_2-CH_2-NH_2)_2Cl_2]^+$, $[CrCl_2(C_2O_4)_2]^{3-}$, $[Fe(H_2O)_4(OH)_2]^+$, $[Fe(NH_3)_2(CN)_4]^-$, $[Co(NH_2-CH_2-CH_2-NH_2)_2(NH_3)Cl]^{2+}$ and $[Co(NH_3)_4(H_2O)Cl]^{2+}$, the number of complex ion(s) that show(s) *cis-trans* isomerism is - [JEE Ad. 2015]
44. Among $[Ni(CO)_4]$, $[NiCl_4]^{2-}$, $[Co(NH_3)_4Cl_2]Cl$, $Na_3[CoF_6]$, Na_2O_2 and CsO_2 , the total number of paramagnetic compounds is - [JEE Ad. 2016]
- (A) 2 (B) 3 (C) 4 (D) 5
45. The number of geometric isomers possible for the complex $[CoL_2Cl_2]^-$ ($L = H_2NCH_2CH_2O^-$) is [JEE Ad. 2016]
46. The geometries of the ammonia complexes of Ni^{2+} , Pt^{2+} and Zn^{2+} , respectively are : [JEE Ad. 2016]
- (A) octahedral, square planar and tetrahedral
- (B) square planar, octahedral and tetrahedral
- (C) tetrahedral, square planar and octahedral
- (D) octahedral, tetrahedral and square planar
47. Addition of excess aqueous ammonia to a pink coloured aqueous solution of $MCl_2 \cdot 6H_2O$ (X) and NH_4Cl gives an octahedral complex Y in the presence of air. In aqueous solution, complex Y behaves as 1 : 3 electrolyte. The reaction of X with excess HCl at room temperature results in the formation of a blue coloured complex Z. The calculated spin only magnetic moment of X and Z is 3.87 B.M., whereas it is zero for complex Y. [JEE Ad. 2017]
- Among the following options, which statements is(are) **CORRECT** ?
- (A) The hybridization of the central metal ion in Y is d^2sp^3
- (B) Z is tetrahedral complex
- (C) Addition of silver nitrate to Y gives only two equivalents of silver chloride
- (D) When X and Z are in equilibrium at $0^\circ C$, the colour of the solution is pink

48. The correct statement(s) regarding the binary transition metal carbonyl compounds is (are)
(Atomic numbers : Fe = 26, Ni = 28) [JEE Ad. 2018]
(A) Total number of valence shell electrons at metal centre in $\text{Fe}(\text{CO})_5$ or $\text{Ni}(\text{CO})_4$ is 16
(B) These are predominantly low spin in nature
(C) Metal - carbon bond strengthens when the oxidation state of the metal is lowered
(D) The carbonyl C-O bond weakens when the oxidation state of the metal is increased
49. The correct option(s) regarding the complex $[\text{Co}(\text{en})(\text{NH}_3)_3(\text{H}_2\text{O})]^{3+}$:- [JEE Ad. 2018]
(en = $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$) is (are)
(A) It has two geometrical isomers
(B) It will have three geometrical isomers if bidentate 'en' is replaced by two cyanide ligands
(C) It is paramagnetic
(D) It absorbs light at longer wavelength as compared to $[\text{Co}(\text{en})(\text{NH}_3)_4]^{3+}$

50. Match each set of hybrid orbitals from LIST-I with complex (es) given in LIST-II.

LIST-I

P. dsp^2 Q. sp^3 R. sp^3d^2 S. d^2sp^3

LIST-II

[JEE Ad. 2018]

1. $[\text{FeF}_6]^{4-}$ 2. $[\text{Ti}(\text{H}_2\text{O})_3\text{Cl}_3]$ 3. $[\text{Cr}(\text{NH}_3)_6]^{3+}$ 4. $[\text{FeCl}_4]^{2-}$ 5. $\text{Ni}(\text{CO})_4$ 6. $[\text{Ni}(\text{CN})_4]^{2-}$

The correct option is

- (A) $\text{P} \rightarrow 5$; $\text{Q} \rightarrow 4,6$; $\text{R} \rightarrow 2,3$; $\text{S} \rightarrow 1$
(B) $\text{P} \rightarrow 5,6$; $\text{Q} \rightarrow 4$; $\text{R} \rightarrow 3$; $\text{S} \rightarrow 1,2$
(C) $\text{P} \rightarrow 6$; $\text{Q} \rightarrow 4,5$; $\text{R} \rightarrow 1$; $\text{S} \rightarrow 2,3$
(D) $\text{P} \rightarrow 4,6$; $\text{Q} \rightarrow 5,6$; $\text{R} \rightarrow 1,2$; $\text{S} \rightarrow 3$
51. Among the species given below, the total number of diamagnetic species is _____.
H atom, NO_2 monomer, O_2^- (superoxide), dimeric sulphur in vapour phase, [JEE Ad. 2018]
 Mn_3O_4 , $(\text{NH}_4)_2[\text{FeCl}_4]$, $(\text{NH}_4)_2[\text{NiCl}_4]$, K_2MnO_4 , K_2CrO_4

ANSWERS KEY

EXERCISE # 0-1

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	A	C	B	C	C	C	D	B	D	B
Que.	11	12	13	14	15	16	17	18	19	20
Ans.	D	B	A	B	A	C	C	D	A	D
Que.	21	22	23	24	25	26	27	28	29	30
Ans.	D	C	B	C	B	B	A	D	A	B
Que.	31	32	33	34	35	36	37	38	39	40
Ans.	D	D	B	C	D	C	C	B	C	C
Que.	41	42	43	44	45	46	47	48	49	50
Ans.	B	C	D	D	D	D	C	B	D	B
Que.	51	52	53	54	55	56	57	58	59	60
Ans.	A	B	A	D	B	D	A	C	B	D
Que.	61	62	63	64	65	66	67	68	69	
Ans.	B	C	C	A	C	C	A	D	A	

EXERCISE # O-2

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	A,B	A,B,D	A,B,C,D	A,B,D	A,B	B,C,D	A,B,C,D	A,B,C	B,C,D	A,B,C,D
Que.	11	12	13	14						
Ans.	B,D	C,D	C,D	B,D						

EXERCISE # S-1

1. (3)	2. (2)	3. (9)	4. (36)
5. (9)	6. (2)	7. (2)	8. (52)
9. (5)	10. (2)		

EXERCISE # S-2

Que.	1				2			
Ans.	(A)-R,	(B)-R	(C)-P	(D)-Q	(A)-P,Q,S	(B)-Q,R,S	(C)-P	(D)-P,Q
Que.	3							
Ans.	(A)-P,S	(B)-T	(C)-Q,R,T	(D)-P,S				

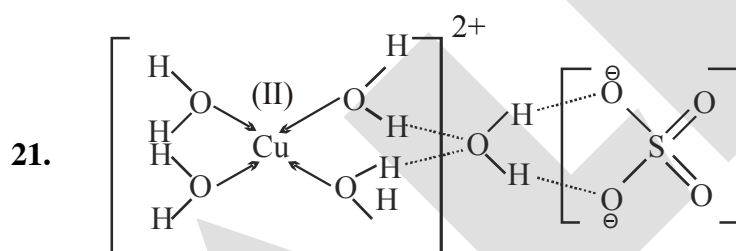
Que.	4	5	6	7	8	9	10	11	12	13
Ans.	B	C	D	D	C	A	C	D	D	A
Que.	14	15	16	17	18					
Ans.	D	B	B	D	D					

EXERCISE # J-MAIN

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	2	3	4	1	3	2	1	3	4	3
Que.	11	12	13	14	15	16	17	18	19	20
	3	1	2	4	4	1	3	4	4	1
Que.	21	22	23	24	25	26	27	28	29	30
Ans.	4	2	3	2	1	1	2	3	3	3
Que.	31	32	33	34	35	36	37	38	39	40
Ans.	1	3	3	4	3	4	4	4	1	3
Que.	41	42	43	44	45	46	47	48	49	50
Ans.	3	3	2	4	4	1	3	3	4	3
Que.	51	52	53	54	55	56	57	58	59	60
Ans.	3	1	2	2	1	2	2	1	3	4
Que.	61	62	63	64	65					
Ans.	3	2	2	4	1					

EXERCISE # J-ADVANCED

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	A	B	D	B	B	B	A	A	C	A
Que.	11	12	13				14	15	16	17
Ans.	A	D	(A)-P,Q,S ; (B)-PR,S ; (C)-Q,S ; (D)-Q,S				C	C	B	B
Que.	18	19	20							
Ans.	A	A	C, D							



Que.	22	23	24	25	26	27	28	29	30	31
Ans.	B	3	C	B	C	6	D	A	C	B
Que.	32	33	34	35						
Ans.	8	B, D	B	4						

36. d^2sp^3 , dsp^2 and sp^3

37. $A \rightarrow [Cr(NH_3)_4ClBr]Cl$

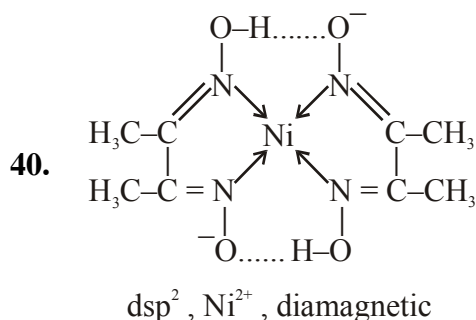
$B \rightarrow [Cr(NH_3)_4Cl_2]Br$

In both Cr is $d^2 sp^3$ hybridised and magnetic moment is $\sqrt{15}$ BM

38. $[NiCl_4]^{2-} \rightarrow sp^3$, $\sqrt{8}$ BM

$[Ni(CN)_4]^{2-} \rightarrow dsp^2$, 0

39. Potassium amminetetrayanidonitrosoniumchromate(I) $\rightarrow d^2sp^3$, octahedral



41. Ans. (4)

42. Ans. (3)

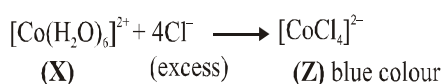
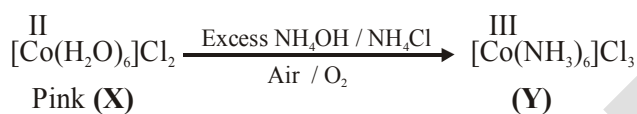
43. Ans. (6)

44. Ans. (B)

45. Ans. (5)

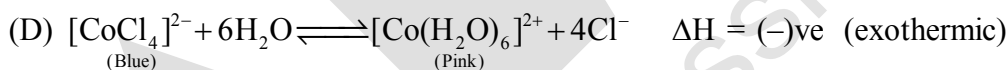
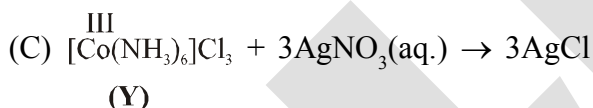
46. Ans. (A)

47. Ans. (A,B,D)



(A) Hybridisation of (Y) is d^2sp^3 as NH_3 is strong field ligand

(B) $[\text{CoCl}_4]^{2-}$ have sp^3 hybridisation as Cl^- is weak field ligand



When ice is added to the solution the equilibrium shifts right hence pink colour will remain predominant

So, correct answer is (A,B& D)

48. Ans.(B,C)

49. Ans.(A,B,D)

50. Ans.(C)

51. Ans.(1)

METALLURGY

□ INTRODUCTION :

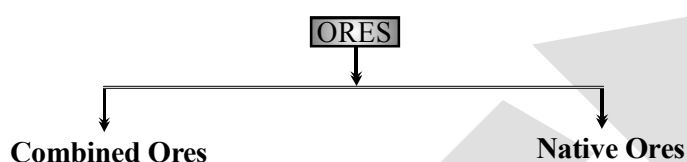
The compound of a metal found in nature is called a **mineral**.

The minerals from which metal can be economically and conveniently extracted are called **ores**.

An ore is usually contaminated with earthy or undesired materials known as **gangue**.

Note : All minerals are not ores but all ores are minerals.

Ores may be classified mainly into following two classes.



(a) **Native ores :** Silver, gold, platinum etc, occur as native ores.

(b) **Combined ores :** They contain the metal in combined form.

(i) **Oxidised ores :** Oxide ores , Carbonate ores, Sulphate ores, Phosphate ores, Silicate ores.

(ii) **Sulphurised ores :** These ores consist of sulphides of metals like iron, lead, zinc, mercury etc.

(iii) **Halide ores :** These ores consist of halides of metals

□ METALLURGY :

The scientific and technological process used for the extraction/isolation of the metal from its ore is called as metallurgy.

The isolation and extraction of metals from their ores involve the following major steps:

(A) Crushing of the ore.

(B) Dressing or concentration of the ore.

(C) Isolation of the crude metal from its ore

(D) Purification or refining of the metal.

(A) **Crushing and Grinding :** The ore is first crushed by crushers and ground to a powder.

(B) **Concentration of the ore :** The removal of unwanted, useless impurities from the ore is called **dressing, concentration or benefaction of ore**.

There are several steps for the concentration of Ores.

(I) By physical separation

(a) Gravity separation (Levigation)

(b) Froth Floatation method

(c) Magnetic separation

(i) Gravity separation or Levigation method :

It is based on the difference in the densities of the gangue and ore particles. This method is generally used for the concentration of oxide and native ores.

(ii) Electromagnetic separation :

It is based on differences in magnetic properties of the ore components.

It is used when either the ore or the impurities associated with it are magnetic in nature.

Examples :

Chromite ore($\text{FeO} \cdot \text{Cr}_2\text{O}_3$) is separated from non-magnetic silicious impurities and cassiterite ore(SnO_2) is separated from magnetic Wolframite ($\text{FeWO}_4 + \text{MnWO}_4$).

(iii) Froth floatation process : This process is based on differential wetting of the ore by oil and gangue by water.

Examples : Galena, PbS (ore of Pb) ; copper pyrites $\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$ or CuFeS_2 (ore of copper) ; zinc blende, ZnS (ore of zinc) etc.

(a) **Frothers :** Oil like pine oil, camphor oil etc., are used as frothers.

(b) **Frothers stablizer :** Aneline & Cressol

(c) **Collectors :** Potassium or sodium ethyl xanthate is used as a collector.

(d) **Activating and depressing agents :** For example galena (PbS) usually contains the minerals namely zinc blende (ZnS) and pyrites (FeS_2) as impurities. Floatation is carried out by using potassium ethyl xanthate (used as a collector) along with NaCN and Na_2CO_3 (used as depressing agent).

(II) By Chemical separation

Some of the ores are concentrated by means of chemical treatment.

Leaching : It involves the treatment of the ore with a suitable reagent. as to make it soluble while impurity remain insoluble. The ore is recovered from the solution by suitable chemical method.

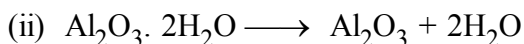
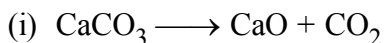
(i) **Bayer's process**

(ii) **Cyanide process**

CALCINATION

Calcination is a process in which ore is heated, generally in the **absence of air**, to expel water from a hydrated oxide or carbon dioxide from a carbonate at temperature below their melting points.

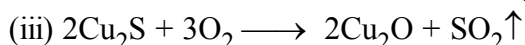
For Example



□ ROASTING

The removal of the excess sulphur contained in sulphide ores by heating **in an excess of air** is called roasting.

(Metal sulphides \longrightarrow Metal oxide + SO_2)



□ REDUCTION OF ORE TO THE METAL

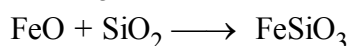
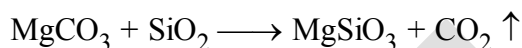
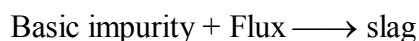
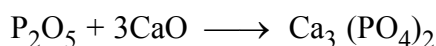
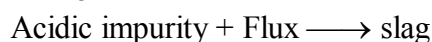
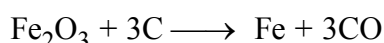
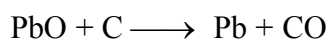
The calcined or roasted ore is then reduced to the metallic state in either of the following ways.

(i) Reduction by Carbon (Smelting)

- Concentrate ore (ore + gangue) + R.A. (carbon) + Flux $[\because \text{R.A.} \Rightarrow \text{Reducing agent}]$



Metal + Slag + gases



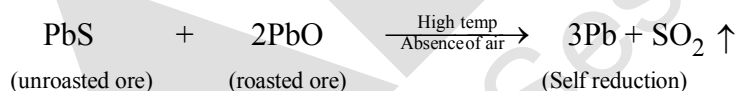
(ii) Self Reduction

Sulphides of certain metals are reduced to metal without using any additional reducing agent. ores of Cu, Pb, Hg etc.

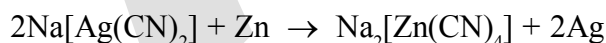
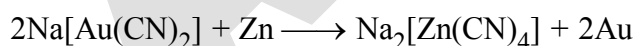
Self Reduction for Pb



(Galena) (air)



(iii) Metal Displacement Method



Sodium tetra cyanozincate

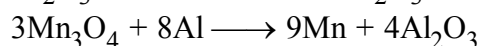
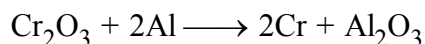
(iv) Electrolytic Reduction

This process is mainly used for the extraction of **highly electropositive metals**.

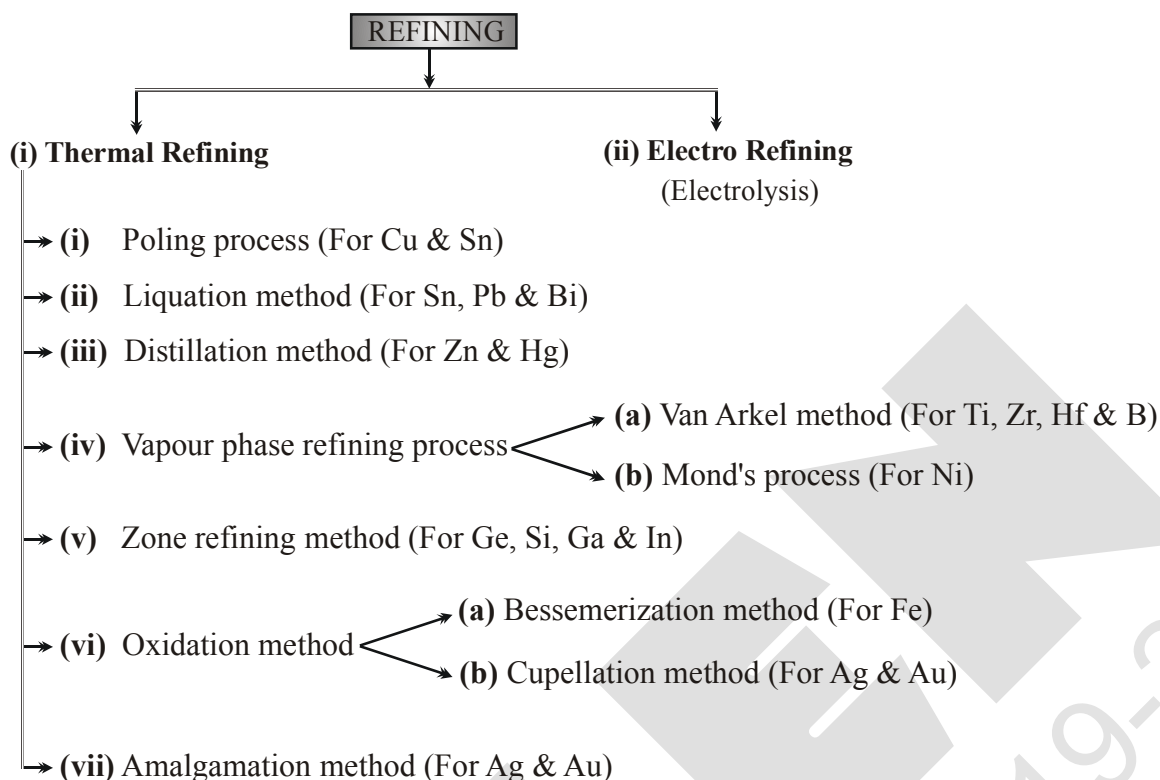
Ex. Na, K, Mg, Ca, Al, etc.

(v) Thermite Reduction or Thermite Process

Al is used as reducing agent in this process. This process is employed in the case of those metals which have very high melting points and are to be extracted from their oxides



REFINING OF METALS



EXTRACTION OF SOME INDIVIDUAL METALS

EXTRACTION OF COPPER

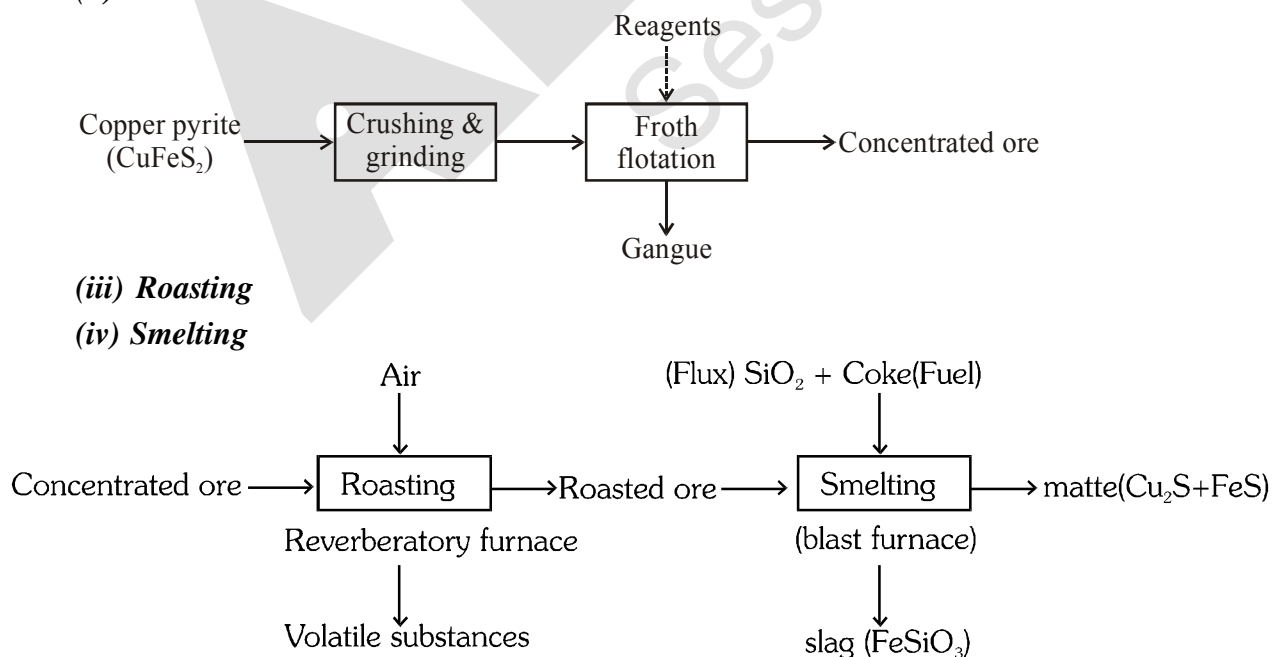
Main Ore : Copper Pyrite (CuFeS_2)

Extraction from pyrites by pyrometallurgical process (Smelting Process)

Some following steps are involved :

(i) Crushing & Grinding

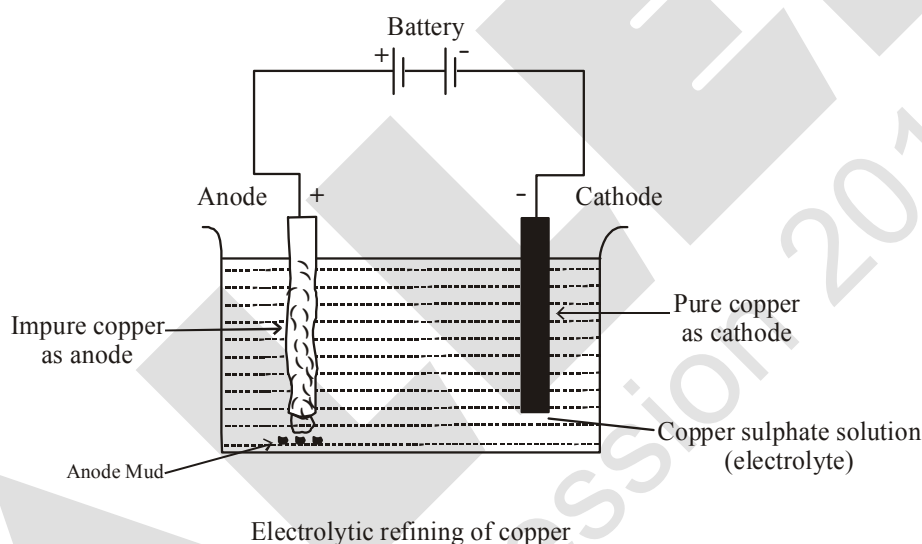
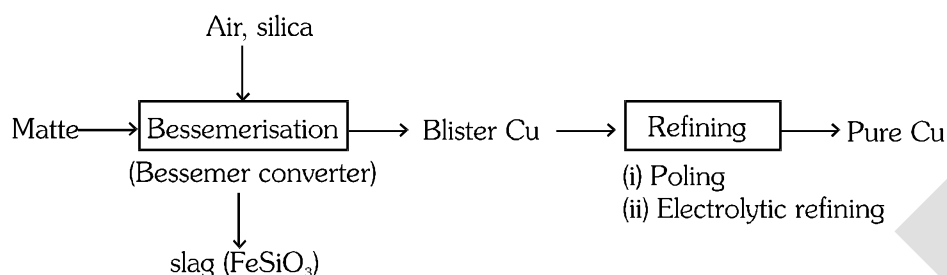
(ii) Concentration



(v) *Self reduction in Bessemer convertor :*

(vi) *Refining of copper :*

(a) Poling (b) Electrolytic refining



Uses :

Copper is the second most useful metal (the first being Iron) because of its stability in air and water and excellent conductivity.

It is used :

- (i) Copper is used for making wires used in electrical industry and for water and steam pipes.
- (ii) For electroplating.
- (iii) As a coinage alloy (with nickel) and in ornaments and jewellery.
- (iv) For the manufacture of alloys like brass (Cu + Zn), bronze (Cu + Sn) German silver (Cu + Zn + Ni) bell metal (Cu + Sn) gun metal (Cu + Sn + Zn), copper coins (Cu + Zn + Sn) etc.

EXTRACTION OF LEAD

Main Ore : Galena (PbS) - There are mainly two types of process used in the extraction of Lead.

Ore - Galena PbS $\begin{cases} \rightarrow \text{(a) Carbon reduction process} \\ \rightarrow \text{(b) Self reduction process} \end{cases}$

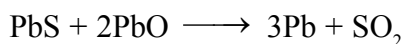
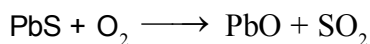
(a) Carbon reduction process (When impurity content is high)

- (i) Crushing & Grinding
- (ii) Concentration by Froth floatation method
- (iii) Roasting process with Lime stone (CaCO_3)
- (iv) Smelting (Carbon reduction method with coke + Fe_2O_3)

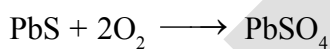
(b) Self reduction process :- (When the impurity content is less)

- (i) Crushing & Grinding
- (ii) Concentration by Froth floatation method
- (iii) Self reduction process

Reaction involved in self reduction :-



Parallel reaction



(c) Refining process :

(a) Liquation

(b) Bett's electrorefining

Anode \rightarrow Impure Pb

Cathode \rightarrow Pure Pb

Electrolyte \rightarrow $\text{Pb}[\text{SiF}_6] + \text{H}_2\text{SiF}_6 + \text{Gelatin}$ (to adjust viscosity)

on the electrolysis Pb is deposited at cathode which give 99.95% pure metal.

EXTRACTION OF ZINC

Occurrence :

Its important minerals are :

- | | |
|-------------------------------|-----------------|
| (i) Zinc blende or black jack | ZnS |
| (ii) Zincite | ZnO |
| (iii) Calamine | ZnCO_3 |

Some following steps are involved :

- (i) Concentration by froth floatation method
- (ii) Roasting/calcination
- (iii) Smelting using carbon reduction

(iv) Electrolytic refining

Anode \rightarrow Impure ZnCathode \rightarrow Thin Al-rodElectrolyte \rightarrow Solution of $\text{ZnSO}_4 + \text{H}_2\text{SO}_4$ (dil.)

on the electrolysis zinc is deposited at cathode. The metal is scrapped off and melted to give 99.95% pure metal.

Uses :

- (i) In making alloys e.g. brass, german silver, elektron (Alloy of Mg with smaller amount of Al, Y, Ag, Gd, Zn) etc.
- (ii) In the extraction of silver and gold by cyanide process.
- (iii) It is also used in large quantities in batteries and dry cells for making cathode container.
- (iv) Zn-Cu couple, Zn-Hg, zinc dust etc. are used as reducing agent in organic reactions.
- (v) large amount of zinc is used for galvanizing iron. Zinc is deposited on the surface of iron articles. This process is called galvanization.
- (vi) It is also used in large quantities in batteries, as a constituent of many alloys, e.g., brass, (Cu 60%, Zn 40%) and german silver (Cu 25-30%, Zn 25-30%, Ni 40-50%).
- (vii) Zinc dust is used as a reducing agent in the manufacture of dye-stuffs, paints, etc.

EXTRACTION OF TIN**Main Ore :**

Cassiterite or Tinstone (SnO_2) + Major impurities [(i) SiO_2 , (ii) Sulphides of Fe & Cu, (iii) $\text{FeWO}_4 + \text{MnWO}_4$]

Some following steps are involved :

(i) **Crushing & Grinding :**(ii) **Concentration :** By gravity separation method.(iii) **Roasting :** Followed by washing(iv) **Electromagnetic separation :**

Thus obtained ore contains 60 – 70% SnO_2 and is called as black tin.

(vi) **Carbon reduction method :** Coke & Lime stone (flux) is used.(vii) **Refining method :** (a) Poling (b) ElectrowinningAnode \rightarrow Impure SnCathode \rightarrow Pure SnElectrolyte \rightarrow (SnSO_4 solution + dil. H_2SO_4)**EXTRACTION OF IRON****Main Ore : Haematite (Fe_2O_3)**

Some following steps are involved :

(i) **Crushing & Grinding :**(ii) **Concentration :** By gravity separation method.(iii) **Roasting :**(iv) **Carbon reduction (Blast furnace) :** Pig iron is obtained from this process(v) **Refining :** Purification of Fe can be done by different method which are as follows :

(a) Puddling Process

(b) Bessemerisation Process

(c) Open hearth Process

(d) L. D. Process

Thus we got pure iron.

Types of Iron

Cast iron or pig iron

It is most impure form of Iron and contains the highest proportion of carbon (2.5 - 4 %) along with traces of S, P, Mn and Si. Cast iron contain 2.5 to 4.3 & pig iron contain 2.5 to 5%.

Wrought iron (Fibrous iron) or malleable iron

It is the purest form of iron and contains minimum amount of carbon (0.12 - 0.25%) and less than 0.5% of other impurities.

Steel

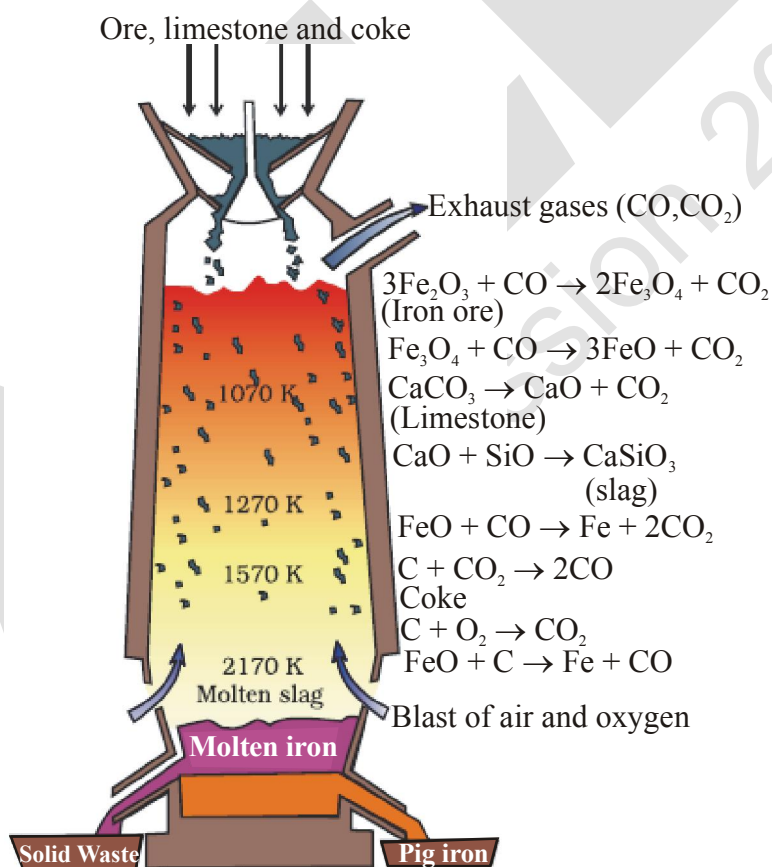
It is the most important form of iron and finds extensive applications. As far as carbon content (impurity) is concerned it is mid-way between cast iron and wrought iron, it contains 0.25- 2% carbon.

Thus all the three forms of iron differ in their carbon contents, both iron and steel are obtained from cast iron.

Order of M.P. Wrought Iron > Steel > Cast Iron or Pig Iron

% of Carbon in different type of Iron

NAME	% of C
(1) Wrought iron	0.1 to 0.25
(2) Steel	0.25 to 2.0
(3) Cast Iron	2.6 to 4.3
(4) Pig Iron	2.3 to 4.6



Blast Furnace

Manufacture of Steel : The addition of different desired impurities into molten pure iron is known as steel making

Heat Treatment of Steel

- (i) **Quenching or hardening** : Steel is heated to red hot temperature (700 to 800°C) and is then cooled suddenly by plunging into either cold water or oil. It makes steel hard and brittle.
- (ii) **Annealing** : The steel is heated to red hot temperature (700 to 800°C) and then cooled slowly. It makes steel soft.
- (iii) **Tempering** : If quenched steel is heated to temperature between 500 to 575 K and then cooled slowly, it becomes quite hard but brittleness disappears. The process is called tempering.

Surface treatment of steel

- (i) **Nitriding** : Process of heating steel at 1000 K in an atmosphere of NH_3 . This gives hard coating of iron nitride on the surface.
- (ii) **Case hardening** : Process of giving a thin coating of hardened steel, by heating steel in contact with charcoal followed quenching in oil.
– It is used for axles of railway wagons.

Uses

- (i) **Cast iron** : It is the most important form of iron, is used for casting stoves, railway sleepers, gutter pipes, toys, etc.
- (ii) It is used in the manufacture of wrought iron and steel.
- (iii) **Wrought iron** : It is used in making anchors, wires, bolts, chains and agricultural implements.
- (iv) **Steel finds a number of uses** : Alloy steel is obtained when other metals are added to it. Nickel steel is used for making cables, automobiles and aeroplane parts, pendulum, measuring tapes, chrome steel for cutting tools and crushing machines, and stainless steel for cycles, automobiles, utensils, pens, etc.

EXTRACTION OF SILVER & GOLD**Extraction of silver :****Occurrence :**

Ag found in free and combined state in nature.

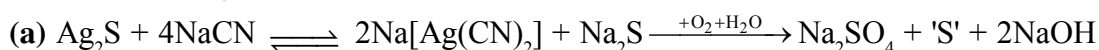
Its main ore is Argentite Ag_2S .

Other ores are

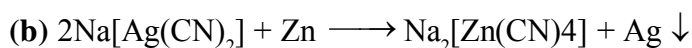
Copper silver glance	—	$\text{Cu}_2\text{S} \cdot \text{Ag}_2\text{S}$
Horn silver	—	AgCl
Argentiferous lead	—	$\text{PbS}(0.01 - 0.1\% \text{ Ag})$

Some steps are involved in the extraction of Silver metal.**(i) Crushing & Grinding :**

(ii) Leaching process : Silver are extracted by the cyanide process (Mc Arthur - Forest process).

Reaction involved :

[$\because \text{O}_2$ is used to make reaction irreversible which remove Na_2S as $\text{Na}_2\text{SO}_4 + \text{S}$]

**(iii) Refining Process :**

Anode	→	Impure Ag
Cathode	→	Pure Ag
Electrolyte	→	$(\text{AgNO}_3 \text{ solution} + \text{dil. HNO}_3)$

Uses :

- (i) It is used in silver plating.
- (ii) Silver foils are used in medicine.
- (iii) Silver amalgam is used for dental filling.
- (iv) Compounds of silver are used in silvering of mirrors ($\text{AgNO}_3 + \text{HCHO} + \text{Red Pb}$), in photography, as laboratory reagents etc.
- (v) Silver is easily alloyed with copper, so it is used in making coins, ornaments, silver ware etc.
- (vi) It gives black spot on skin due to decomposition so it is also used as hair dye and ink.

Extraction of Gold :

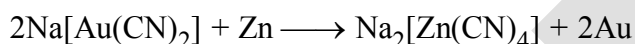
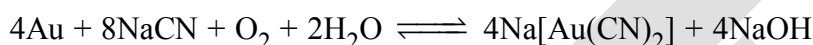
Occurrence : Au found in free (native) state in nature.

Same steps as are involved in the extraction of Silver metal.

(i) **Crushing & Grinding :**

(ii) **Leaching process :** Gold are extracted by the cyanide process (Mc Arthur - Forest process).

Reaction involved :



(iii) **Refining Process :**

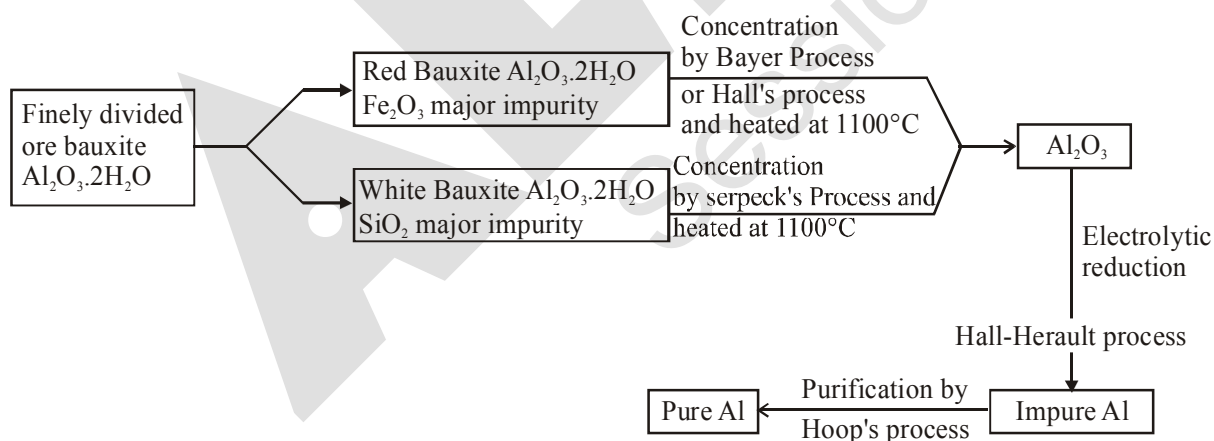
Anode	→	Impure Au
Cathode	→	Pure Au
Electrolyte	→	(AuCl_3 solution + dil. HCl)



EXTRACTION OF ALUMINIUM :

Ore - Bauxite $\text{AlO}_x(\text{OH})_{3-2x}$ (where $0 < x < 1$)

Flow chart of Al from $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ (Bauxite)



Uses

- (i) Aluminium foils are used as wrappers for chocolates.
- (ii) The fine dust of the metal is used in paints and lacquers.
- (iii) Aluminium, being highly reactive, is also used in the extraction of chromium and manganese from their oxides.
- (iv) Wires of aluminium are used as electricity conductors.
- (v) Alloys containing aluminium, being light, are very useful.

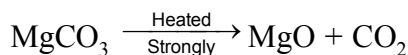
□ EXTRACTION OF MAGNESIUM :

(i) From Carnallite :

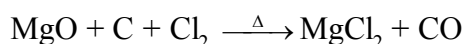
The ore is dehydrated in a current of hydrogen chloride and the mixture of fused chlorides is electrolysed.

(ii) From Magnesite :

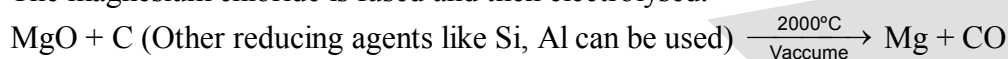
The concentrated ore is calcined at higher temperature



The calcined ore is heated with coke in a current of dry chlorine gas.



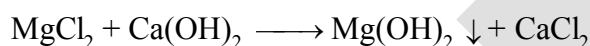
The magnesium chloride is fused and then electrolysed.



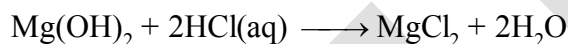
(iii) From Sea water (Dow's process) :

Sea water contains 0.13% magnesium as chloride and sulphate. It involves following steps.

(a) Precipitation of magnesium as magnesium hydroxide by slaked lime :

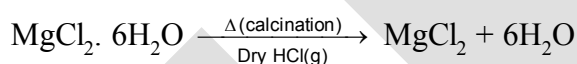


(b) Preparation of hexahydrated magnesium chloride



The solution on concentration and crystallisation gives the crystals of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$

(c) Preparation of anhydrous magnesium chloride



It is not made anhydrous by simple heating because it gets hydrolysed



(d) Electrolysis of fused anhydrous MgCl_2

(i) Electrolyte : Molten $\text{MgCl}_2 + \text{NaCl} + \text{CaCl}_2$

(ii) Anode : Graphite electrode

(iii) Cathode : Iron cell (steel container)

Reaction occurs :

The molten mixture is electrolysed. Magnesium is liberated at the cathode (iron pot) and chlorine is evolved at graphite anode.

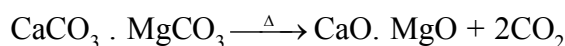


At cathode : $\text{Mg}^{2+} + 2\text{e}^- \longrightarrow \text{Mg(99\% pure)}$;

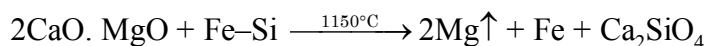
At anode : $2\text{Cl}^- \longrightarrow \text{Cl}_2 + 2\text{e}^-$

(iv) From Dolomite : In the Pidgeon Process Mg is Produced.

The concentrated ore is calcined at higher temperature



It is then reduced by ferrosilicon at 1273 K under reduced pressure.



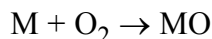
❑ THERMODYNAMICS OF REDUCTION PROCESSES (ELLINGHAM DIAGRAM)

The extraction of metals from their oxides using carbon or other metals, and by thermal decomposition, involves a number of points which merit detailed discussion.

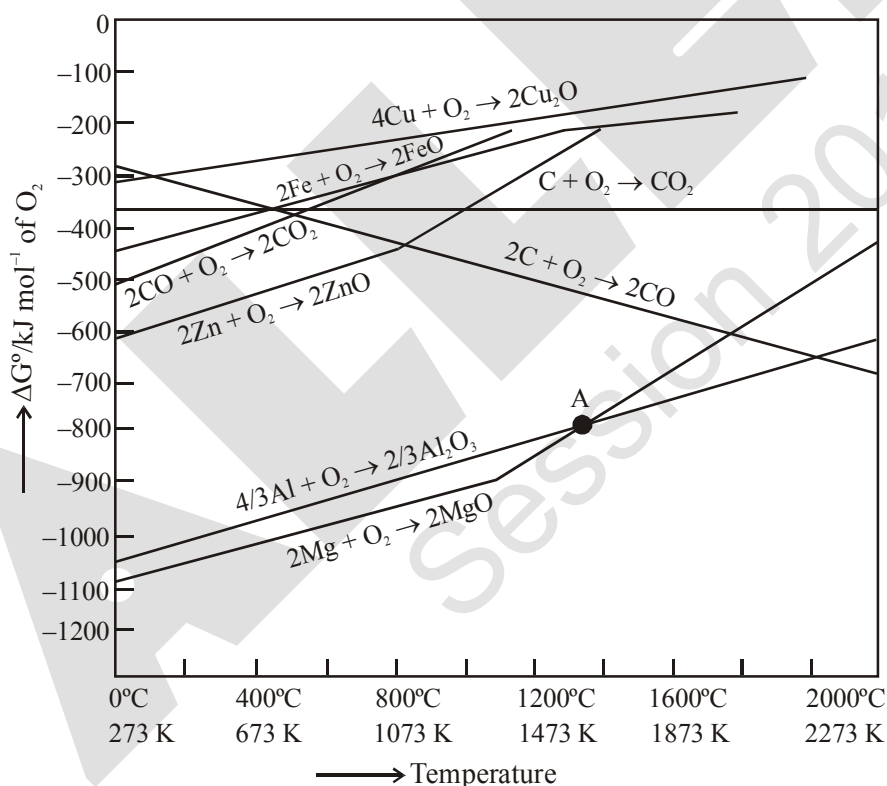
For a spontaneous reaction, the free energy change ΔG must be negative.

$$\Delta G = \Delta H - T\Delta S$$

ΔH is the enthalpy change during the reaction, T is the absolute temperature, and ΔS is the change in entropy during the reaction. Consider a reaction such as the formation of an oxide:



Dioxygen is used up in the course of this reaction. Gases have a more random structure (less ordered) than liquids or solids. Consequently gases have a higher entropy than liquids or solids. In this reaction S the entropy or randomness decreases, the hence ΔS is negative. Thus if the temperature is raised then $T\Delta S$ becomes more negative. Since $T\Delta S$ is subtracted in the equation, then ΔG becomes less negative. Thus the free energy changed increases with an increase of temperature.



The free energy changes that occur when one gram molecule of a common reactant (in this case dioxygen) is used may be plotted graphically against temperature for a number of reactions of metals of their oxides. This graph is shown in figure and is called an Ellingham diagram (for oxides). Similar diagrams can be produced for one gram molecule of sulphur, giving an Ellingham diagram for sulphides, and similarly for halides.

The Ellingham diagram for oxides shows several important features:

- (i) The graph for metal oxide all slope upwards, because the free energy change increases with an increase of temperature as discussed above.
- (ii) The free energy changes all follows a straight line unless the materials metal or vaporize.
- (iii) When the temperature is raised, a point will be reached where the graph crosses the $\Delta G = 0$ line. Below this temperature the free energy of formation of the oxide is negative, so the oxide is stable. Above this temperature the free of formation of the oxide is positive, and the oxide becomes unstable, and should decompose into the metal and dioxygen.
- (iv) Any metal will reduce the oxide of other metals which lie above it in the Ellingham diagram because the free energy will become more negative by an amount equal to the different between the two graphs at that particular temperature.

Limitations of Ellingham Diagram

- (i) The graph simply indicates whether a reaction is possible or not i.e., the tendency of reduction with a reducing agent is indicated. This is so because it is based only on the thermodynamic concepts. It does not say about the kinetics of the reduction process (Cannot answer questions like how fast it could be ?).
- (ii) The interpretation of ΔG^\ominus is based on $K(\Delta G^\ominus = -RT \ln K)$. Thus it is presumed that the reactants of products are in equilibrium.

Aluminium	1. Bauxite, $\text{Al}_2\text{O}_3 \cdot x \text{H}_2\text{O}$ 2. Cryolite, Na_3AlF_6	Electrolysis of Al_2O_3 dissolved in molten Na_3AlF_6	For the extraction, a good source of electricity is required.
Iron	1. Haematite, Fe_2O_3 2. Magnetite, Fe_3O_4	Reduction of the oxide with CO and coke in Blast furnace	Temperature approaching 2170 K is required.
Copper	1. Copper pyrites, CuFeS_2 2. Copper glance, Cu_2S 3. Malachite, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ 4. Cuprite, Cu_2O	Roasting of sulphide partially and reduction	It is self reduction in a specially designed converter. The reduction takes place easily. Sulphuric acid leaching is also used in hydrometallurgy from low grade ores.
Zinc	1. Zinc blende or Sphalerite, ZnS 2. Calamine, ZnCO_3 3. Zincite, ZnO	Roasting followed by reduction with coke	The metal may be purified by fractional distillation.

GENERAL PRINCIPLES & PROCESSES OF ISOLATION OF ELEMENTS

EXERCISE # O-I

ONLY ONE OPTION IS CORRECT.

ORES

- Which of the following does not contain Mg:
(A) magnetite (B) magnesite (C) asbestos (D) carnallite
- Which of the following is not an ore:
(A) malachite (B) calamine (C) stellite (D) cerussite
- Carnallite does not contain
(A) K (B) Ca (C) Mg (D) Cl
- Among the following statements, the incorrect one is
(A) calamine and siderite are carbonate ores (B) argentite and cuprite are oxide ores
(C) zinc blende and pyrites are sulphide ores (D) malachite and azurite are ores of copper
- Select the correct statement :
(A) Magnetite is an ore of manganese (B) Pyrolusite is an ore of lead
(C) Siderite is carbonate ore of iron (D) FeS_2 is rolled gold
- "Fool's gold" is
(A) iron pyrites (B) horn silver (C) copper pyrites (D) bronze
- Assertion :** Platinum and gold occur in native state in nature.
Reason : Platinum and gold are noble metals.
(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
(C) Statement-1 is true, statement-2 is false.
(D) Statement-1 is false, statement-2 is true.

CONCENTRATION METHODS

- $\text{Ag}_2\text{S} + \text{NaCN} + \text{Zn} \longrightarrow \text{Ag}$
This method of extraction of Ag by complex formation and then its displacement is called:
(A) Parke's method (B) McArthur-Forest method
(C) Serpeck method (D) Hall's method
- Which one of the following is not a method of concentration of ore?
(A) gravity separation (B) froth floating process
(C) electromagnetic separation (D) smelting
- Chemical leaching is useful in the concentration of:
(A) copper pyrites (B) bauxite (C) galena (D) cassiterite
- In froth-floatation process, pine oil functions as
(A) activator (B) frother (C) collector (D) agitator

12. Collectors are the substances which help in attachment of an ore particle to air bubble in froth. A popular collector used industrially is
(A) sodium ethyl xanthate (B) sodium xenate
(C) sodium pyrophosphate (D) sodium nitroprusside
13. In the cyanide process involving extraction of silver, zinc is used industrially as a(an)
(A) oxidising agent (B) reducing agent
(C) solvent (D) solvating agent
14. During initial treatment, preferential wetting of ore by oil and gangue by water takes place in
(A) Levigation (gravity separation) (B) Froth floatation
(C) Leaching (D) Bessemerisation
15. An non-magnetic ore containing the impurity of FeCr_2O_4 is concentrated by
(A) magnetic-separation (B) gravity separation
(C) froth-floatation method (D) electrostatic method
16. The beneficiation of the sulphide ores is usually done by
(A) Electrolysis (B) Smelting process
(C) Metal displacement method (D) Froth flotation method
17. The process of the isolation of a metal by dissolving the ore in aqueous solution of suitable chemical reagent followed by precipitation of the metal by a more electropositive metal is called:
(A) hydrometallurgy (B) electrometallurgy
(C) zone refining (D) electrorefining
18. Froth floatation process for concentration of ores is an illustration of the practical application of:
(A) Adsorption (B) Absorption
(C) Coagulation (D) Sedimentation
19. **Assertion :** Sulphide ores are concentrated by froth floatation process.
Reason : Pine oil acts as a frothing agent in froth floatation process.
(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
(C) Statement-1 is true, statement-2 is false.
(D) Statement-1 is false, statement-2 is true.
20. **Assertion :** Wolframite impurities are separated from cassiterite by electromagnetic separation.
Reason : Cassiterite being magnetic is attracted by the magnet and forms a separate heap.
(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
(C) Statement-1 is true, statement-2 is false.
(D) Statement-1 is false, statement-2 is true.

CALCINATION/ROASTING

- 21.** Calcination is the process of heating the ore:
- (A) in inert gas (B) in the presence of air
(C) in the absence of air (D) in the presence of CaO and MgO
- 22.** When roasting is carried out :
- (i) Sulphide ore is converted into oxide and sulphate
(ii) remove water of hydration
(iii) the ore melts (iv) arsenic and sulphur impurities are removed
- Of these statements:
- (A) (i), (ii) and (iii) are correct (B) (i) and (iv) are correct
(C) (i), (ii) and (iv) are correct (D) (ii), (iii) and (iv) are correct

REDUCTION PROCESS

23. In the aluminothermite process, Al acts as
(A) An oxidising agent (B) A flux
(C) A reducing agent (D) A solder
24. **Assertion :** Al is used as a reducing agent in aluminothermy.
Reason : Al has a lower melting point than Fe, Cr and Mn.
(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
(C) Statement-1 is true, statement-2 is false.
(D) Statement-1 is false, statement-2 is true.
25. Formation of metallic copper from the sulphide ore in the commercial thermo-metallurgical process essentially involves which one of the following reaction:
- (A) $\text{Cu}_2\text{S} + \frac{3}{2}\text{O}_2 \longrightarrow \text{Cu}_2\text{O} + \text{SO}_2$; $\text{CuO} + \text{C} \longrightarrow \text{Cu} + \text{CO}$
(B) $\text{Cu}_2\text{S} + \frac{3}{2}\text{O}_2 \longrightarrow \text{Cu}_2\text{O} + \text{SO}_2$; $2\text{Cu}_2\text{O} + \text{Cu}_2\text{S} \longrightarrow 6\text{Cu} + \text{SO}_2$
(C) $\text{Cu}_2\text{S} + 2\text{O}_2 \longrightarrow \text{CuSO}_4$; $\text{CuSO}_4 + \text{Cu}_2\text{S} \longrightarrow 3\text{Cu} + 2\text{SO}_2$
(D) $\text{Cu}_2\text{S} + \frac{3}{2}\text{O}_2 \longrightarrow \text{Cu}_2\text{O} + \text{SO}_2$; $\text{Cu}_2\text{O} + \text{CO} \longrightarrow 2\text{Cu} + \text{CO}_2$
26. The element which could be extracted by electrolytic reduction of its oxide dissolved in a high temperature melt is:
(A) sodium (B) magnesium (C) fluorine (D) aluminium
27. In which of the following isolations no reducing agent is required:
(A) iron from haematite (B) Tin from cassiterite
(C) mercury from cinnabar (D) zinc from zinc blende

PURIFICATION METHODS

28. A metal has a high concentration into the earth crust and whose oxides cannot be reduced by carbon. The most suitable method for the extraction of such metal is
 (A) Alumino thermite process (B) Electrolysis process
 (C) Van-Arkel's process (D) Cupellation
29. **Assertion :** Alkali metals can not be prepared by the electrolysis of their chlorides in aqueous solution
Reason : Reduction potentials of alkali metals cations is much lower than that of H_2O .
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
 (C) Statement-1 is true, statement-2 is false.
 (D) Statement-1 is false, statement-2 is true.
30. **Assertion :** Magnesium can be prepared by the electrolysis of aq. $MgCl_2$.
Reason : The reduction potential of Mg^{2+} is much lower than that of H_2O .
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
 (C) Statement-1 is true, statement-2 is false.
 (D) Statement-1 is false, statement-2 is true.
31. Bessemerisation is carried out for
 I : Fe, II : Cu, III : Al, IV : silver
 (A) I, II (B) II, III (C) III, IV (D) I, III
32. In the extraction of nickel by Mond process, the metal is obtained by:
 (A) electrochemical reduction (B) thermal decomposition
 (C) chemical reduction by aluminium (D) reduction by carbon
33. Formation of $Ni(CO)_4$ and subsequent its decomposition into Ni and CO (recycled) makes basis of Mond's process

$$Ni + 4CO \xrightarrow{T_1} Ni(CO)_4 \xrightarrow{T_2} Ni + 4CO$$
 T_1 and T_2 are:
 (A) $100^\circ C$, $50^\circ C$ (B) $50^\circ C$, $100^\circ C$ (C) $50^\circ C$, $230^\circ C$ (D) $230^\circ C$, $50^\circ C$
34. Zone refining is based on the principle of
 (A) fractional distillation (B) fractional crystallisation
 (C) partition coefficient (D) chromatographic separation
35. Si and Ge used for semiconductors are required to be of high purity and hence purified by
 (A) zone-refining (B) electrorefining
 (C) Van-Arkel's process (D) cupellation process
36. Which process of purification is represented by the following equation :

$$Ti(\text{Impure}) + 2I_2 \xrightarrow{250^\circ C} TiI_4 \xrightarrow{1400^\circ C} Ti(\text{Pure}) + 2I_2$$
 (A) Cupellation (B) Poling (C) Van-Arkel Process (D) Zone refining
37. Which of the following employ(s) thermal decomposition of volatile iodide compounds?
 (A) Thermite process (B) Hall's process (C) Van-Arkel's process (D) Mond's process

38. The method of zone refining of metals is based on the principle of:
 (A) Greater mobility of the pure metal than that of impurity.
 (B) Higher melting point of the impurity than that of the pure metal.
 (C) Greater noble character of the solid metal than that of the impurity
 (D) Greater solubility of the impurity in the molten state than in the solid
39. **Assertion :** Titanium is purified by Van-Arkel method.
Reason : Ti reacts with I_2 to form volatile TiI_4 which decomposes at 1673 K to give pure Ti.
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
 (C) Statement-1 is true, statement-2 is false.
 (D) Statement-1 is false, statement-2 is true.
40. **Assertion :** Nickel is purified by the thermal decomposition of nickel tetracarbonyl.
Reason : Nickel is a transition element.
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
 (C) Statement-1 is true, statement-2 is false.
 (D) Statement-1 is false, statement-2 is true.
41. Refining of silver is done by:
 (A) liquation (B) poling (C) cupellation (D) van Arkel method
42. Mercury is purified by:
 (A) Passing through dilute HNO_3 (B) Distillation
 (C) Distribution (D) Vapour phase refining
43. **Assertion :** Lead, tin and bismuth are purified by liquation method.
Reason : Lead, tin and bismuth have low m.p. as compared to impurities.
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
 (C) Statement-1 is true, statement-2 is false.
 (D) Statement-1 is false, statement-2 is true.
44. When an impurity in a metal has greater affinity for oxygen and is more easily oxidised than the metal itself. Then, the metal is refined by
 (A) cupellation (B) zone-refining (C) distillation (D) electrolytic process

EXTRACTION OF METALS

45. Which of the following process is not associated with recovery of the silver -
 (A) As a side product in electrolytic refining of copper
 (B) Parke's process in which Zn is used to extract silver by solvent extraction from molten lead
 (C) By reaction of silver sulphide with KCN and then reaction of soluble complex with Zn
 (D) By boiling $Na[Ag(CN)_2]$ aq.
46. Blister Cu is about:
 (A) 60% Cu (B) 90% Cu (C) 98% Cu (D) 100% Cu

47. Iron obtained from blast furnace is:
(A) wrought iron (B) cast iron (C) pig iron (D) steel
48. Which of the following term is not related to Al-extraction
(A) Serpek's process (B) Hall-Heroult process
(C) Thermite process (D) Hoop's process
49. Dow's process
(A) involves purification of copper (B) involves extraction of magnesium
(C) gives metal chloride as product (D) gives pure Na as product
50. Silica is added to roasted copper ores during extraction in order to remove
(A) cuprous sulphide (B) ferrous oxide (C) ferrous sulphide (D) cuprous oxide
51. Addition of high proportions of manganese makes steel useful in making rails of railroads, because manganese
(A) gives hardness to steel (B) helps the formation of oxides of iron
(C) can remove oxygen and sulphur (D) can show highest oxidation state of +7
52. In the commercial electrochemical process for aluminium extraction the electrolyte used is
(A) $\text{Al}(\text{OH})_3$ in NaOH solution (B) an aqueous solution of $\text{Al}_2(\text{SO}_4)_3$
(C) a molten mixture of Al_2O_3 , Na_3AlF_6 & CaF_2 (D) a molten mixture of Al_2O_3 and $\text{Al}(\text{OH})_3$
53. Blister copper is refined by stirring molten impure metal with green logs of wood because such a wood liberates hydrocarbon gases (like CH_4). This process X is called _____ and the metal contains impurities of Y is _____.
(A) X = cupellation, Y = CuO_2 (B) X = poling, Y = Cu_2O
(C) X = poling, Y = CuO (D) X = cupellation, Y = CuO
54. A piece of steel is heated until redness and then plunged into cold water or oil. This treatment of steel makes it
(A) soft and malleable (B) hard but not brittle
(C) more brittle (D) hard and brittle
55. Modern method of steel manufacturing is
(A) open hearth process (B) L.D. Process
(C) Bessemerisation (D) Cupellation
56. During electrolytic reduction of alumina, two auxiliary electrolytes X and Y are added to increase the electrical conductance and lower the temperature of melt in order to making fused mixture very conducting. X and Y are
(A) cryolite and flourspar (B) cryolite and alum
(C) alum and flourspar (D) flourspar and bauxite
57. For extraction of sodium from NaCl, the electrolytic mixture $\text{NaCl} + \text{KCl} + \text{CaCl}_2$ is used. During extraction process, only sodium is deposited on cathode but K and Ca do not because
(A) Na is more reactive than K and Ca
(B) Na is less reactive than K and Ca
(C) NaCl is less stable than Na_3AlF_6 and CaCl_2
(D) the discharge potential of Na^+ is less than that of K^+ and Ca^{2+} ions.

58. Railway wagon axles are made by heating iron rods embedded in charcoal powder. This process is known as:
 (A) Sherardising (B) Annealing (C) Tempering (D) Case hardening
59. In the extraction of copper from its sulphide ore the metal is formed by the reduction of Cu_2O with:
 (A) FeS (B) CO (C) Cu_2S (D) SO_2
60. Carnallite on electrolysis gives:
 (A) Ca and Cl_2 (B) Na and CO_2 (C) Al and Cl_2 (D) Mg and Cl_2

MISCELLANEOUS

61. Which of the following statement is correct regarding Cu-extraction
 (A) In the smelting step carbon reduction takes places
 (B) During partial roasting Cu_2S remains almost unaffected
 (C) In Bessemer converter, only self reduction occur, not slag formation
 (D) Blister forms in the blister Cu is due to dissolved CO_2
62. Refractory materials are generally used in furnaces because
 (A) they are chemically inert (B) they can withstand high temperature
 (C) they do not contain impurities (D) they decrease melting point of ore
63. Which of the following statements is correct regarding the slag formation during the extraction of a metal like copper or iron.
 (A) The slag is lighter and has lower melting temperature than the metal
 (B) The slag is heavier and has lower melting temperature than the metal
 (C) The slag is lighter and has higher melting temperature than the metal
 (D) The slag is heavier and has higher melting temperature than the metal
64. **Assertion :** Generally in smelting, roasted/cacinated ore is heated with powdered coke in presence of a flux.
Reason : Oxides are reduced to metals by C or CO. Impurities are removed as slag.
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
 (C) Statement-1 is true, statement-2 is false.
 (D) Statement-1 is false, statement-2 is true.
65. **Assertion :** Magnesias and quick lime are used as basic flux.
Reason : MgO and CaO can withstand very high temperatures.
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
 (C) Statement-1 is true, statement-2 is false.
 (D) Statement-1 is false, statement-2 is true.
66. **Assertion :** Wolframite impurity is separated from SnO_2 by magnetic separation
Reason : Tin stone is ferromagnetic, therefore attracted by magnet.
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
 (C) Statement-1 is true, statement-2 is false.
 (D) Statement-1 is false, statement-2 is true.

EXERCISE # O-2

ONE OR MORE THAN ONE OPTION MAY BE CORRECT

- Which of the following is(are) sulphide ores?
(A) Argentite (B) Galena (C) Anglesite (D) Copper glance
- Which of the following is(are) regarded as iron ores?
(A) Haematite (B) Magnetite (C) Limonite (D) Copper pyrites

CONCENTRATION

- Which of the following ores is(are) concentrated by froth floatation?
(A) haematite (B) galena (C) copper pyrite (D) azurite
- Which of the following ores is (are) concentrated industrially by froth floatation?
(A) Copper pyrites (B) Galena (C) Dolomite (D) Carnallite
- Leaching is used for the concentration of:
(A) Red bauxite (B) Haematite (C) Gold ore (D) Silver ore

CALCINATION/ROASTING

- Calcination and roasting processes of ores to form their oxides are beneficial
(A) to convert ores into porous form so that their reduction becomes easier
(B) as impurities like S, As, Sb, are removed
(C) as organic impurities are removed.
(D) as the ores are converted into oxide form which makes the reduction easier
- Which of the following reaction(s) occur during calcination?
(A) $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$ (B) $4\text{FeS}_2 + 11\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 + 8\text{SO}_2$
(C) $2\text{Al}(\text{OH})_3 \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$ (D) $\text{CuS} + \text{CuSO}_4 \rightarrow 2\text{Cu} + 2\text{SO}_2$
- Which of the following is true for calcination of a metal ore?
(A) It makes the ore more porous
(B) The ore is heated to a temperature when fusion just begins
(C) Hydrated salts lose their water of crystallisation
(D) Impurities of S, As and Sb are removed in the form of their volatile oxides.
- Roasting can be performed in
(A) blast furnace (B) reverberatory furnace
(C) electric furnace (D) None of these

REDUCTION

- Carbon reduction method is employed for commercial extraction of metal from amongst these :
(A) haematite (B) cassiterite (C) iron pyrite (D) corundum
- Auto reduction process is used in extraction of
(A) Cu (B) Hg (C) Al (D) Fe
- Which of the following reduction reactions are actually employed in commercial extraction of metals?
(A) $\text{Fe}_2\text{O}_3 + 2\text{Al} \rightarrow \text{Al}_2\text{O}_3 + 2\text{Fe}$
(B) $\text{Cr}_2\text{O}_3 + 2\text{Al} \rightarrow \text{Al}_2\text{O}_3 + 2\text{Cr}$
(C) $2\text{Na}[\text{Au}(\text{CN})_2] + \text{Zn} \rightarrow \text{Na}_2[\text{Zn}(\text{CN})_4] + 2\text{Au}$
(D) $\text{Cu}_2\text{S} + \text{Pb} \rightarrow \text{Cu} + \text{PbS} \downarrow$

PURIFICATION

- 13.** In the manufacturing of metallic sodium by fused salt-electrolysis method (Down's process), small amount of CaCl_2 that added is known as auxiliary electrolyte and is used to
- (A) improve the electrical conductance (B) decrease the melting point of electrolyte
(C) stabilise the metallic sodium (D) increase the temperature of electrolysis
- 14.** Poling is employed in refining of
- (A) iron (B) copper (C) tin (D) lead
- 15.** Zone refining is used for purification of
- (A) Ge (B) Si (C) Ga (D) In
- 16.** Metal(s) which does/do not form amalgam is/are
- (A) Fe (B) Pt (C) Zn (D) Au
- 17.** Metals which can be commercially extracted by smelting process
- (A) Pb (B) Fe (C) Zn (D) Mg

EXTRACTION OF METALS

18. Hoop's process of purification of aluminium involves formation of layers during electrolysis. It involves
- (A) the three layers have same densities but different materials.
(B) the three layers have different densities
(C) the upper layer is of pure aluminium which acts as a cathode
(D) the bottom layer is of impure aluminium which acts as an anode and middle layer consists of cryolite and BaF_2 .
19. Metallurgical process of zinc involves roasting of zinc sulphide followed by reduction. Metallic zinc distills over as it is volatile and impurities like Cu, Pb and Fe gets condensed. The crude metal obtained is called spelter, which may be purified by
- (A) electrolysis process (B) fractional distillation
(C) polling (D) heating with iodine
20. Which of the following process (es) are used for purification of Bauxite ore?
- (A) Hall's process (B) Serpeck's process (C) Baeyer's process (D) Mond's process
21. Common impurities present in Bauxite are
- (A) CuO (B) ZnO (C) Fe_2O_3 (D) SiO_2
22. Calcium silicate slag formed in extraction of iron
- (A) prevents the reoxidation of molten iron.
(B) catalyses the combustion of carbon.
(C) reduces CO_2 to CO at the bottom of the furnace.
(D) is used in cement industry.
23. Amphoteric nature of aluminium is employed in which of the following process for extraction of aluminium?
- (A) Baeyer's process (B) Hall's process
(C) Serpeck's process (D) Dow's process
24. The chief reaction(s) occurring in blast furnace during extraction of iron from haematite is(are)
- (A) $\text{Fe}_2\text{O}_3 + 3\text{CO} \rightarrow 2\text{Fe} + 3\text{CO}_2$ (B) $\text{FeO} + \text{SiO}_2 \rightarrow \text{FeSiO}_3$
(C) $\text{Fe}_2\text{O}_3 + \text{C} \rightarrow 2\text{Fe} + 3\text{CO}$ (D) $\text{CaO} + \text{SiO}_2 \rightarrow \text{CaSiO}_3$

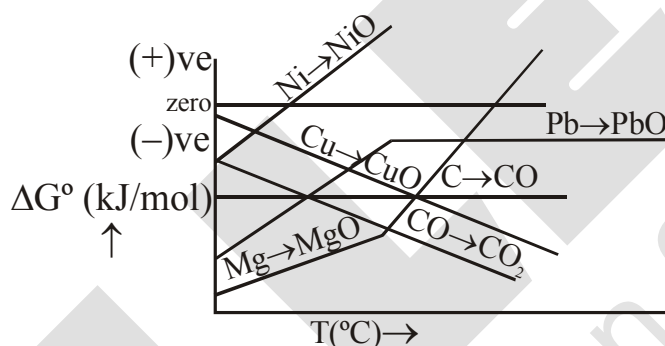
25. Which of the following are true for electrolytic extraction of aluminium
(A) cathode material contains graphite (B) anode material contains graphite
(C) cathode reacts away forming CO_2 (D) anode reacts away forming CO_2
26. During extraction of copper, it is obtained in the form of molten *matte*. Which of the following is **not true**?
(A) *matte* is further treated in Bessemer's converter
(B) molten *matte* is electrolysed
(C) It is treated with a blast of air and sand
(D) It is dissolved in CuSiF_6 and crystallised.
27. The major role of fluorspar (CaF_2) which is added in small quantities in the electrolytic reduction of alumina dissolved in fused cryolite (Na_3AlF_6) is
(A) as a catalyst
(B) to make the fused mixture very conducting
(C) to lower the melting temperature of the mixture
(D) to decrease the rate of oxidation of carbon at the anode.
28. Which of the following reaction does not occur in blast furnace during extraction of iron :
(A) $\text{CaO} + \text{SiO}_2 \longrightarrow \text{CaSiO}_3$ (B) $\text{Fe}_2\text{O}_3 + 3\text{CO} \longrightarrow 2\text{Fe} + 3\text{CO}_2$
(C) $\text{FeO} + \text{SiO}_2 \longrightarrow \text{FeSiO}_3$ (D) $\text{FeO} \longrightarrow \text{Fe} + \frac{1}{2}\text{O}_2$

MISCELLANEOUS

29. Which of the following employ downward movement of ore due to gravity?
(A) Gravity separation (B) Froth floatation
(C) Blast furnace (D) Bessemer's converter
30. The **CORRECT** statements are :
(A) generally the calcination and roasting is done in blast furnace
(B) the sandy and rocky materials associated with ore are called matrix
(C) froth floatation process is suitable for sulphide ores
(D) substance that reacts with gangue to form fusible mass is called slag

EXERCISE # S-1

- Find the number of ore which are concentrated by magnetic separation method.
Haemetite, Cassiterite, Copper Glance, Chromite, Cinnabar
- Find the number of metals which are commercially extracted by carbon reduction method
Pb, Fe, Zn, Mg, Al, Na, Au, Ag
- The number of following pairs is correctly matched
 - Van Arkel method – Zirconium
 - Mond Process – Titanium
 - Froth Floatation Method – Cerussite
 - Distillation method – Zinc
 - Poling Process – Copper
 - amalgamation – Gold
- Find the number of curves which are wrongly presented in the Ellingham diagram.

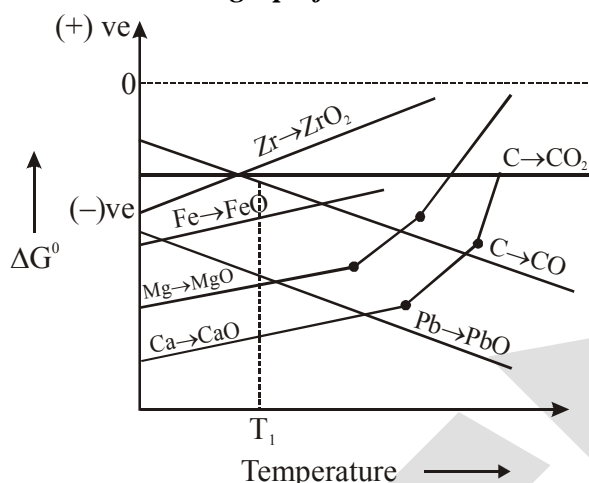


- How many of the following minerals containing Mg.
Magnetite, Carnallite, Epsom salt, Siderite
- Find out the number of minerals given below contain iron as Fe(II).
Haematite, Magnetite, Limonite, Siderite, Chromite, Wolframite
- Amongst the following ores, the total number of oxide ores are
Siderite, Magnetite, Haematite, Malachite, Zincite, Cuprite
- Amongst the following, total number of sulphide ores are
Calamine, Sphalertie, Copper pyrites, Copper glance, Iron pyrites, Bauxite
- How many of the following ores of silver ?
Hornsilver, Cerrusite, Chalcopyrite, Galena, Anglesite, Argentite

EXERCISE # S-2

COMPREHENSION AND MATCH THE COLUMN
ELLINGHAM DIAGRAM

Paragraph for 1 to 3



- Which of the above curve is wrongly presented -
(A) $C \rightarrow CO_2$ (B) $Pb \rightarrow PbO$ (C) $Zr \rightarrow ZrO_2$ (D) $Mg \rightarrow MgO$
- Which of the above metal oxide is having minimum thermal decomposition temperature.
(A) CaO (B) FeO (C) ZrO_2 (D) MgO
- Which of the following metal's oxide can be reduced by Fe as reducing agent at temperature (T_1)
(A) Zr (B) Ca (C) Mg (D) None of these

PURIFICATION METHOD

Paragraph for 4 to 5

At high temperature carbon reacts with water to produce a mixture of carbon monoxide, CO and hydrogen, H_2 .



CO is separated from H_2 and then used to separate nickel from cobalt by forming a volatile compound, nickel tetracarbonyl, $Ni(CO)_4$.



- How many moles of $Ni(CO)_4$ could be obtained from the CO produced by the reaction of 75.0g of carbon? Assume 100% reaction and 100% recovery in both steps.
(A) 6.25 (B) 1.563 (C) 3.125 (D) 25.0
- Formation of volatile $Ni(CO)_4$ and its subsequent heating gives pure Ni. Process is called -
(A) Hall (B) Dow (C) Serpeck (D) Mond

MISCELLANEOUS

Match Column

- Match Column-I with Column-II

Column-I (Metals)

- (A) Iron & copper
(B) Zirconium & Titanium
(C) Lead & Tin
(D) Copper & Tin

Column-II (Method used for refining)

- (P) Poling
(Q) Bessemerisation
(R) Van-Arkel
(S) Liquation

7. Match the following choosing one item from column X and the appropriate item from column Y.

Column -X

- (A) Zinc from ZnCO_3
(B) Lead from PbS
(C) Cu from CuFeS_2
(D) Tin from cassiterite

Column-Y

- (P) Calcination
(Q) Removal of iron
(R) Froth floatation process
(S) Poling

8. Match column (I) (process) with column (II) (electrolyte)

Column (I) (process)

- (A) Downs cell
(B) Dow's sea water process
(C) Hall-Heroult

Column (II) (electrolyte)

- (P) fused MgCl_2
 (Q) fused $(\text{Al}_2\text{O}_3 + \text{Na}_3\text{AlF}_6 + \text{CaF}_2)$
 (R) fused $(40\% \text{ NaCl} + 60\% \text{ CaCl}_2)$
 (S) $(\text{AlN} + \text{C} + \text{N}_2)$

9. Match column - I with column - II

Column - I (Property)

- (A) Explosive
(B) Self-reduction
(C) Ferrimagnetic material
(D) Verdigris

Column - II (Element/compound)

- (P) Cu
(Q) Fe_3O_4
(R) $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{Cu}(\text{OH})_2$
(S) $\text{Pb}(\text{NO}_3)_2$

10. Match column - I and column - II and select the correct answer using the codes given below the lists:

Column - I

- (A) Cyanide process
(B) Flotation process
(C) Electrolytic reduction
(D) Zone refining

Column - II

- (P) Ultrapure Ge
(Q) Dressing of HgS
(R) Extraction of Al
(S) Extraction of Au

11. Match the items of Column I with items of Column II and assign the correct code :

Column I

- (P) Blistered Cu
(Q) Blast furnace
(R) Reverberatory furnace
(S) Hall-Heroult process

Column II

- (1) Aluminium
- (2) $2\text{Cu}_2\text{O} + \text{Cu}_2\text{S} \rightarrow 6\text{Cu} + \text{SO}_2$
- (3) Iron
- (4) $\text{FeO} + \text{SiO}_2 \rightarrow \text{FeSiO}_3$
- (5) $2\text{Cu}_3\text{S} + 3\text{O}_2 \rightarrow 2\text{Cu}_2\text{O} + 2\text{SO}_2$

Code : (A) $P \rightarrow (2) ; Q \rightarrow (3) ; R \rightarrow (4) ; S \rightarrow (1)$ (B) $P \rightarrow (1) ; Q \rightarrow (2) ; R \rightarrow (3) ; S \rightarrow (5)$
(C) $P \rightarrow (5) ; Q \rightarrow (4) ; R \rightarrow (3) ; S \rightarrow (2)$ (D) $P \rightarrow (4) ; Q \rightarrow (5) ; R \rightarrow (3) ; S \rightarrow (2)$

Answer Q.12, Q.13 and Q.14 by appropriately matching the information given in the three columns of the following table.

Column - I Extraction of metal	Column - II Methods for Reduction	Column - III Refining Method
(1) $\text{SnO}_2 \rightarrow \text{Sn}$	(i) Carbon Reduction	(P) Poling
(2) $\text{Al}_2\text{O}_3 \rightarrow \text{Al}$	(ii) Hydrometallurgic Reduction	(Q) Electrolytic Refining
(3) $\text{Cu}_2\text{S} \rightarrow \text{Cu}$	(iii) Electrolytic Reduction	(R) Distillation
(4) $\text{ZnS} \rightarrow \text{Zn}$	(iv) Self-Reduction	(S) Puddling Process

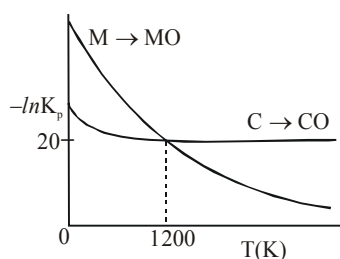
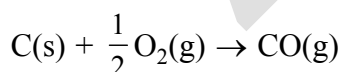
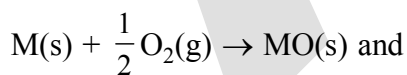
12. Which of the following is **NOT** correctly matched?
 (A) (1), (iv), (S) (B) (3), (iv), (P) (C) (4), (i), (R) (D) (2), (iii), (Q)
13. Which of the following match is the **CORRECT** reduction and purification methods for Zn
 (A) (i), (R) (B) (iv), (S) (C) (iv), (P) (D) None of these
14. Which of the following set of code shows the **CORRECT** similarity with the extraction processes for Pb?
 (A) (1), (ii), (S) (B) (4), (iii), (P) (C) (2), (iii), (Q) (D) (3), (iv), (Q)

EXERCISE # JEE-MAINS

1. Aluminium is extracted by the electrolysis of :- [AIEEE-2002]
 (1) Bauxite (2) Alumina
 (3) Alumina mixed with molten cryolite (4) Molten cryolite
2. Pyrolusite is a/an :- [AIEEE-2002]
 (1) Oxide ore (2) Sulphide ore (3) Carbide ore (4) Not an ore
3. Which one of the following ores is best concentrated by froth-flotation method : [AIEEE-2004]
 (1) Galena (2) Cassiterite (3) Magnetite (4) Malachite
4. Which of the following factors is of no significance for roasting sulphide ores to the oxides and not subjecting the sulphide ores to carbon reduction directly ? [AIEEE-2008]
 (1) Metal sulphides are thermodynamically more stable than CS_2
 (2) CO_2 is thermodynamically more stable than CS_2
 (3) Metal sulphides are less stable than the corresponding oxides
 (4) CO_2 is more volatile than CS_2
5. Which method of purification is represented by the following equation : [AIEEE-2012]

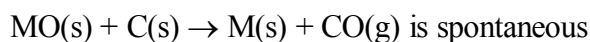
$$Ti(s) + 2I_2(g) \xrightarrow{523K} TiI_4(g) \xrightarrow{1700K} Ti(s) + 2I_2(g)$$
 (1) Van Arkel (2) Zone refining (3) Cupellation (4) Poling
6. The substance used as froth stabilisers in froth-flotation process is : [J-Mains-2012 (On line)]
 (1) Copper sulphate (2) Aniline
 (3) Sodium cyanide (4) Potassium ethyl xanthate
7. Which of the oxide groups among the following cannot be reduced by carbon :- [J-Mains-2012 (On line)]
 (1) Fe_3O_4 , ZnO (2) PbO, Fe_3O_4 (3) Cu_2O , SnO_2 (4) CaO, K_2O
8. In Goldschmidt aluminothermic process which of the following reducing agents is used : [J-Mains-2013 (On line)]
 (1) Calcium (2) Coke (3) Sodium (4) Al-powder
9. Calcination is the process in which :
 (1) Ore is heated strongly below its melting point in the presence of excess of air and is used for the conversion of carbonates and hydrated oxide ores to their respective oxides.
 (2) Ore is heated strongly below its melting point in the absence or limited supply of air and is used for conversion of sulphide ores to their respective oxides
 (3) Ore is heated strongly below its melting point either in the limited supply or absence of air and is used to convert carbonates and hydrated oxide ores to their respective oxides
 (4) Ore is heated strongly above its melting point in the limited supply of air to convert sulphide ores to their respective oxides.

10. The metal that cannot be obtained by electrolysis of an aqueous solution of its salts is :
[JEE-MAINS-2014]
- (1) Cu (2) Cr (3) Ag (4) Ca
11. The form of iron obtained from blast furnace is :
[J-Mains-2014 (On line)]
- (1) Steel (2) Wrought Iron (3) Cast Iron (4) Pig iron
12. In the context of the Hall-Heroult process for the extraction of Al, which of the following statements is false ?
[JEE-MAINS-2015]
- (1) Al^{3+} is reduced at the cathode to form Al
(2) Na_3AlF_6 serves as the electrolyte
(3) CO and CO_2 are produced in this process
(4) Al_2O_3 is mixed with CaF_2 which lowers the melting point of the mixture and brings conductivity
13. Galvanization is applying a coating of :-
[JEE-MAINS-2016]
- (1) Zn (2) Pb (3) Cr (4) Cu
14. Which one of the following ores is best concentrated by froth floatation method ?
[JEE-MAINS-2016]
- (1) Malachite (2) Magnetite (3) Siderite (4) Galena
15. What will occur if a block of copper metal is dropped into a beaker containing a solution of 1M ZnSO_4 ?
[JEE-MAINS (Online) - 2016]
- (1) The copper metal will dissolve and zinc metal will be deposited
(2) No reaction will occur
(3) The copper metal will dissolve with evolution of oxygen gas
(4) The copper metal will dissolve with evolution of hydrogen gas
16. The plot shows the variation of $-\ln K_p$ versus temperature for the two reactions ?



Identify the correct statement :

- (1) At $T > 1200\text{ K}$, carbon will reduce MO(s) to M(s)
- (2) At $T < 1200\text{ K}$, oxidation of carbon is unfavourable.
- (3) Oxidation of carbon is favourable at all temperature
- (4) At $T < 1200\text{ K}$, the reaction



17. In the leaching method, bauxite ore is digested with a concentrated solution of NaOH that produces 'X'. When CO_2 gas is passed through the aqueous solution of 'X', a hydrated compound 'Y' is precipitated. 'X' and 'Y' respectively are :-
[JEE MAIN ONLINE. 2018]

- (1) $\text{Na[Al(OH)}_4\text{]}$ and $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$
- (2) Al(OH)_3 and $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$
- (3) $\text{Na[Al(OH)}_4\text{]}$ and $\text{Al}_2(\text{CO}_3)_3 \cdot x\text{H}_2\text{O}$
- (4) Na AlO_2 and $\text{Al}_2(\text{CO}_3)_3 \cdot x\text{H}_2\text{O}$

18. When metal 'M' is treated with NaOH , a white gelatinous precipitate 'X' is obtained, which is soluble in excess of NaOH . Compound 'X' when heated strongly gives an oxide which is used in chromatography as an adsorbent. The metal 'M' is
[JEE MAIN OFFLINE. 2018]

- (1) Ca
- (2) Al
- (3) Fe
- (4) Zn

19. In the extraction of copper from its sulphide ore, metal is finally obtained by the oxidation of cuprous sulphide with :-
[JEE MAIN ONLINE. 2018]

- (1) CO
- (2) Cu_2O
- (3) Fe_2O_3
- (4) SO_2

EXERCISE # JEE-ADVANCED

- Carnallite does not contain
(A) K (B) Ca (C) Mg (D) Cl
- During initial treatment, preferential wetting of ore by oil and gangue by water takes place in
(A) Levigation (gravity separation) (B) Froth floatation
(C) Leaching (D) Bessemerisation
- Which of the following is true for calcination of a metal ore?
(A) It makes the ore more porous
(B) The ore is heated to a temperature when fusion just begins
(C) Hydrated salts lose their water of crystallisation
(D) Sulphur in sulphides is oxidised to SO_2
(E) Heating with carbon leads to better calcination
- In the commercial electrochemical process for aluminium extraction, the electrolyte used as :
[JEE-1999]
(A) $\text{Al}(\text{OH})_3$ in NaOH solution (B) an aqueous solution of $\text{Al}_2(\text{SO}_4)_3$
(C) a molten mixture of Al_2O_3 and Na_3AlF_6 (D) a molten mixture of $\text{AlO}(\text{OH})$ and $\text{Al}(\text{OH})_3$
- The chemical process in the production of steel from haematite ore involve: [2000 Qualifying]
(A) reduction (B) oxidation
(C) reduction followed by oxidation (D) oxidation followed by reduction
- Electrolytic reduction of alumina to aluminium by Hall-Heroult process is carried out:
(A) in the presence of NaCl [2000 Qualifying]
(B) in the presence of fluorite
(C) in the presence of cryolite which forms a melt with lower melting temperature
(D) in the presence of cryolite which forms a melt with higher melting temperature
- The chemical composition of "slag" formed during the smelting process in the extraction of copper is :
[2001 Qualifying]
(A) $\text{Cu}_2\text{O} + \text{FeS}$ (B) FeSiO_3 (C) CuFeS_2 (D) $\text{Cu}_2\text{S} + \text{FeO}$
- Which of the following processes is used in extractive metallurgy of magnesium? [2002 Qualifying]
(A) Fused salt electrolysis (B) Self reduction
(C) Aqueous solution electrolysis (D) Thermite reduction
- In the process of extraction of gold, [2003 Qualifying]
Roasted gold ore + $\text{CN}^- + \text{H}_2\text{O} \xrightarrow{\text{O}_2} [\text{X}] + \text{OH}^-$
 $[\text{X}] + \text{Zn} \longrightarrow [\text{Y}] + \text{Au}$
Identify the complexes [X] and [Y] :
(A) $\text{X} = [\text{Au}(\text{CN})_2]^-$, $\text{Y} = [\text{Zn}(\text{CN})_4]^{2-}$ (B) $\text{X} = [\text{Au}(\text{CN})_4]^{3-}$, $\text{Y} = [\text{Zn}(\text{CN})_4]^{2-}$
(C) $\text{X} = [\text{Au}(\text{CN})_2]^-$, $\text{Y} = [\text{Zn}(\text{CN})_6]^{4-}$ (D) $\text{X} = [\text{Au}(\text{CN})_4]^-$, $\text{Y} = [\text{Zn}(\text{CN})_4]^{2-}$
- The methods chiefly used for the extraction of lead and tin from their ores are respectively :
[JEE-2004]
(A) self reduction and carbon reduction (B) self reduction and electrolytic reduction
(C) carbon reduction and self reduction (D) cyanide process and carbon reduction

11. Which ore contains both iron and copper ? [JEE-2004]
 (A) Cuprite (B) Chalcocite (C) Chalcopyrite (D) Malachite
12. Extraction for zinc from zinc blende is achieved by : [JEE-2007]
 (A) electrolytic reduction
 (B) roasting followed by reduction with carbon
 (C) roasting followed by reduction with another metal
 (D) roasting followed by self-reduction
13. Native silver metal forms a water soluble complex with a dilute aqueous solution of NaCN in the presence of :- [JEE-2008]
 (A) nitrogen (B) oxygen
 (C) carbon dioxide (D) argon

Paragraph for questions 14 to 16

Copper is the most noble of the first row transition metals and occurs in small deposits in several countries. Ores of copper include chalcantite ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), atacamite ($\text{Cu}_2\text{Cl}(\text{OH})_3$), cuprite (Cu_2O), copper glance (Cu_2S) and malachite ($\text{Cu}_2(\text{OH})_2\text{CO}_3$). However, 80% of the world copper production comes from the ore chalcopyrite (CuFeS_2). The extraction of copper from chalcopyrite involves partial roasting, removal of iron and self-reduction. [JEE-2010]

14. Partial roasting of chalcopyrite produces :-
 (A) Cu_2S and FeO (B) Cu_2O and FeO (C) CuS and Fe_2O_3 (D) Cu_2O and Fe_2O_3
15. Iron is removed from chalcopyrite as :-
 (A) FeO (B) FeS (C) Fe_2O_3 (D) FeSiO_3
16. In self-reduction, the reducing species is :-
 (A) S (B) O^{2-} (C) S^{2-} (D) SO_2
17. Match the extraction processes listed in column I with metals listed in column II. [JEE-2006]

Column I

- (A) Self reduction
 (B) Carbon reduction
 (C) Complex formation and displacement by metal
 (D) Decomposition of iodide

Column II

- (P) Lead
 (Q) Silver
 (R) Copper
 (S) Boron

18. Match the conversions in **Column I** with the type(s) of reaction(s) given in **Column II**. Indicate your answer by darkening the appropriate bubbles of the 4×4 matrix given in the ORS. [JEE-2008]

Column I

- (A) $\text{PbS} \rightarrow \text{PbO}$
 (B) $\text{CaCO}_3 \rightarrow \text{CaO}$
 (C) $\text{ZnS} \rightarrow \text{Zn}$
 (D) $\text{Cu}_2\text{S} \rightarrow \text{Cu}$

Column II

- (P) Roasting
 (Q) Calcination
 (R) Carbon reduction
 (S) Self reduction

19. In extractive metallurgy of zinc partial fusion of ZnO with coke is called _____ and reduction of the ore to the molten metal is called _____ (smelting, calcining, roasting, sintering). [JEE-1988]

20. Extraction of metal from the ore cassiterite involves [JEE-2011]
 (A) carbon reduction of an oxide ore (B) self-reduction of a sulphide ore
 (C) removal of copper impurity (D) removal of iron impurity
21. Oxidation states of the metal in the minerals haematite and magnetite, respectively, are [JEE-2011]
 (A) II, III in haematite and III in magnetite (B) II, III in haematite and II in magnetite
 (C) II in haematite and II, III in magnetite (D) III in haematite and II, III in magnetite
22. In the cyanide extraction process of silver from argentite ore, the oxidizing and reducing agents used are : [JEE-2012]
 (A) O_2 and CO respectively. (B) O_2 and Zn dust respectively.
 (C) HNO_3 and Zn dust respectively. (D) HNO_3 and CO respectively.
23. Sulfide ores are common for the metals - [JEE-2013]
 (A) Ag, Cu and Pb (B) Ag, Cu and Sn (C) Ag, Mg and Pb (D) Al, Cu and Pb
24. The carbon-based reduction method is **NOT** used for the extraction of [JEE-2013]
 (A) tin from SnO_2 (B) Iron from Fe_2O_3
 (C) aluminium from Al_2O_3 (D) magnesium from $MgCO_3 \cdot CaCO_3$
25. Upon heating with Cu_2S , the reagent(s) that give copper metal is/are [JEE Adv. 2014]
 (A) $CuFeS_2$ (B) CuO (C) Cu_2O (D) $CuSO_4$
26. Copper is purified by electrolytic refining of blister copper. The correct statement(s) about this process is (are) [JEE Adv. 2015]
 (A) Impure Cu strip is used as cathode
 (B) Acidified aqueous $CuSO_4$ is used as electrolyte
 (C) Pure Cu deposits at cathode
 (D) Impurities settle as anode-mud
27. Match the anionic species given in Column-I that are present in the ore(s) given in Column-II [JEE Adv. 2015]
- | Column-I | Column-II |
|---------------|---------------|
| (A) Carbonate | (P) Siderite |
| (B) Sulphide | (Q) Malachite |
| (C) Hydroxide | (R) Bauxite |
| (D) Oxide | (S) Calamine |
| | (T) Argentite |
28. Extraction of copper from copper pyrite ($CuFeS_2$) involves [JEE Adv. 2016]
 (A) crushing followed by concentration of the ore by froth-flotation
 (B) removal of iron as slag
 (C) self-reduction step to produce 'blister copper' following evolution of SO_2
 (D) refining of 'blister copper' by carbon reduction
29. Galena (an ore) is partially oxidized by passing air through it at high temperature. After some time, the passage of air is stopped, but the heating is continued in a closed furnace such that the contents undergo self-reduction. The weight (in kg) of Pb produced per kg of O_2 consumed is _____. [JEE ADV. 2018]
 (Atomic weights in $g\ mol^{-1}$: O = 16, S = 32, Pb = 207)

ANSWER KEY

EXERCISE # O-I

1. (A)	2. (C)	3. (B)	4. (B)	5. (C)	6. (A)
7. (A)	8. (B)	9. (D)	10. (B)	11. (B)	12. (A)
13. (B)	14. (B)	15. (A)	16. (D)	17. (A)	18. (A)
19. (B)	20. (C)	21. (C)	22. (C)	23. (C)	24. (B)
25. (B)	26. (D)	27. (C)	28. (B)	29. (A)	30. (D)
31. (A)	32. (B)	33. (C)	34. (B)	35. (A)	36. (C)
37. (C)	38. (D)	39. (A)	40. (B)	41. (C)	42. (B)
43. (A)	44. (A)	45. (D)	46. (C)	47. (C)	48. (C)
49. (B)	50. (B)	51. (A)	52. (C)	53. (B)	54. (D)
55. (B)	56. (A)	57. (D)	58. (D)	59. (C)	60. (D)
61. (B)	62. (B)	63. (A)	64. (A)	65. (B)	66. (C)

EXERCISE # O-II

1. (A,B,D)	2. (A,B,C)	3. (B,C)	4. (A,B)	5. (A,C,D)	6. (A,B,C,D)
7. (A, C)	8. (A, C)	9. (A, B)	10. (A, B)	11. (A,B)	12. (B, C)
13. (A,B)	14. (B,C)	15. (A,B,C, D)	16. (A,B)	17. (A,B, C)	18. (B,C,D)
19. (A,B)	20. (A,B,C)	21. (C,D)	22. (A, D)	23. (A,B)	24. (A, D)
25. (A,B,D)	26. (B,D)	27. (B,C)	28. (C,D)	29. (A,C)	30. (B, C)

EXERCISE # S-1

1. (3)	2. (3)	3. (4)	4. (4)	5. (2)	6. (4)
7. (4)	8. (4)	9. (2)			

EXERCISE # S-2

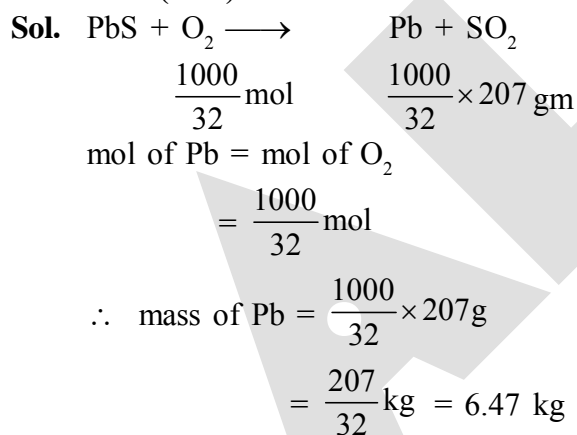
1. (B)	2. (C)	3. (A)	4. (B)	5. (D)	
6. (A) Q; (B) R; (C) S; (D) P	7. (A) → P, (B) → R ; (C) → Q, R, S (D) → Q, S				
8. (A) R ; (B) P; (C) Q	9. (A) S ; (B) P; (C) Q; (D) R				
10. (A) S ; (B) Q ; (C) R ; (D) P	11. (A)	12. (A)	13. (A)	14. (D)	

EXERCISE # JEE-MAINS

- | | | | | | |
|---------|---------|---------|---------|---------|---------|
| 1. (3) | 2. (1) | 3. (1) | 4. (3) | 5. (1) | 6. (2) |
| 7. (4) | 8. (4) | 9. (3) | 10. (4) | 11. (4) | 12. (2) |
| 13. (1) | 14. (4) | 15. (2) | 16. (3) | 17. (1) | 18. (2) |
| 19. (2) | | | | | |

EXERCISE # JEE-ADVANCED

- | | | | | | |
|---|---------|-------------------------|---|---------------|---------|
| 1. (B) | 2. (B) | 3. (A,C) | 4. (C) | 5. (C) | 6. (C) |
| 7. (B) | 8. (A) | 9. (A) | 10. (A) | 11. (C) | 12. (B) |
| 13. (B) | 14. (A) | 15. (D) | 16. (C) | | |
| 17. (A) – P, R ; (B) – P ; (C) – Q ; (D) – S | | | 18. (A) – P ; (B) – Q ; (C) – P, R ; (D) – P, S | | |
| 19. Sintering , Smelting | | 20. (A, D) or (A, C, D) | | 21. (D) | |
| 22. (B) | 23. (A) | 24. (C, D) | 25. (B, C, D) | 26. (B, C, D) | |
| 27. (A) – P , Q , S ; (B) – T ; (C) – Q , R ; (D) – R | | | | 28. (A, B, C) | |

29. Ans. (6.47)

NURTURE COURSE
IONIC EQUILIBRIUM

IONIC EQUILIBRIUM

1. INTRODUCTION

Ionic equilibrium deals with the equilibrium of any substance with its ions in solution. The substance producing ions are called electrolytes.

According to conductivity, substances are of two types :

(i) Non-Conductor :

Those substances which do not show the flow of current or electricity.

Ex. Non - metals, plastic rubber, wood, etc.

Exception – Graphite is a non-metal but shows conductivity due to motion of free electrons.

(ii) Conductors :

Those substances which show conductivity or flow of current are called conductors. These are of 2 types :

(a) Metallic or electronic conductors :

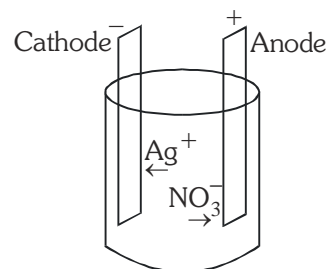
Those conductor which show conductivity due to motion of free electrons. Resistance increases with temperature.

Ex. All metals, Graphite

(b) Ionic or electrolytic conductors :

Those conductors which show conductivity due to movement of free ions. Ions are in free state in the solutions of ionic compounds. On passing electric current through the solution, ions move towards oppositely charged electrodes, i.e., the cation moves towards cathode (negative electrode) and the anion moves towards anode (positive electrode).

The current flows through the solution due to the movement of the ions. Resistance decrease with temperature.



According to strength, ionic conductors are of two types :

(i) Strong electrolyte :

Those ionic conductors which are completely ionized in aqueous solution are called as strong electrolyte.

For strong electrolyte the value of degree of dissociation is 100%.

i.e. : $\alpha = 1$

- Ex.** (a) Strong acid \rightarrow H_2SO_4 , HCl , HNO_3 , HClO_4 , H_2SO_5 , HBr , HI , HBrO_4 , HIO_4 , RSO_3H
 (b) Strong base \rightarrow KOH , NaOH , $\text{Ba}(\text{OH})_2$, CsOH , RbOH
 (c) All soluble salts \rightarrow NaCl , KCl , CuSO_4 ,

(ii) Weak electrolytes :

Those electrolytes which are partially ionized in aqueous solution are called as weak electrolytes. For weak electrolytes the value of α is less than one.

- Ex.** (a) Weak acid : HCN , CH_3COOH , HCOOH , H_2CO_3 , H_3PO_3 , H_3PO_2 , etc.
 (b) Weak base : NH_4OH , $\text{Cu}(\text{OH})_2$, $\text{Zn}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$, etc.

1.2 DEGREE OF DISSOCIATION / IONISATION

- When an electrolyte is dissolved in a solvent (H_2O), it spontaneously dissociates into ions.
- It may dissociate partially ($\alpha < 1$) or sometimes completely ($\alpha \cong 1$)
- The degree of dissociation (α) of an electrolyte is the fraction of mole of the electrolyte that has dissociated under the given conditions.

$$\alpha = \frac{\text{No. of moles dissociated}}{\text{No. of moles taken initially}}$$

1.3 FACTORS AFFECTING THE VALUE OF DEGREE OF DISSOCIATION:

- (i) **Dilution** : $\alpha \propto \sqrt{V}$. So on dilution, α increases
- (ii) **Temperature** : On increasing temperature, ionization increases so, α increases
- (iii) **Nature of electrolyte** :

(a) Strong electrolyte

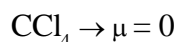
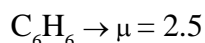
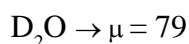
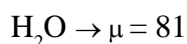
$$\alpha = 100\%$$

(b) Weak electrolyte

$$\alpha \ll 100\%$$

- (iv)
- Nature of solvent**
- :

If dielectric constant, μ , of solvent increases, then the value of α increases.



Ex.1 Which one has greater α_1 or α_2 for the following equation :



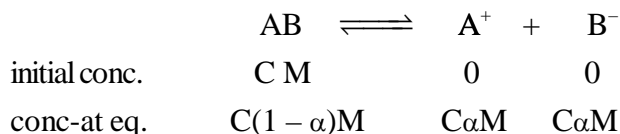
Sol. Dielectric constant of H_2O is more than that of D_2O , so $\alpha_1 > \alpha_2$

- (v)
- Mixing of Ions**
- :

Common ion Effect	Odd ion Effect
$NH_4OH \rightleftharpoons NH_4^+ + OH^-$ On mixing NH_4Cl $NH_4Cl \rightarrow NH_4^+ + Cl^-$ Due to mixing of common ion, concentration of ammonium ion will increase therefore equilibrium will shift in backward direction means α decreases.	$NH_4OH \rightleftharpoons NH_4^+ + OH^-$ On mixing HCl $HCl \rightarrow H^+ + Cl^-$ Due to reaction of OH^- ions with H^+ ion, concentration of OH^- will decrease \therefore Equilibrium will shift in forward direction means α increases.

1.4 OSTWALD'S DILUTION LAW (FOR WEAK ELECTROLYTE)

- For a weak electrolyte $A^+ B^-$ dissolved in water, if α is the degree of dissociation then



Then according to law of mass action,

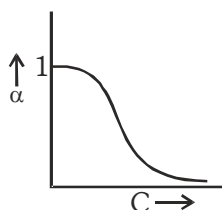
$$K_{\text{diss}} = \frac{[A^+][B^-]}{[AB]} = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)} = \text{dissociation constant of the weak electrolyte.}$$

$$\left[C = \frac{1}{V}, \text{ then } V = 1/C \text{ (volume of solution in which 1 mole is present) is called dilution, so } K_{\text{diss}} = \frac{\alpha^2}{(1-\alpha)V} \right]$$

If α is negligible in comparison to unity, $1 - \alpha \approx 1$. so $K_{\text{diss}} = \alpha^2 C \Rightarrow \alpha = \sqrt{\frac{K_{\text{diss}}}{C}} = \sqrt{K_{\text{diss}} V}$

$$\alpha \propto \frac{1}{\sqrt{\text{concentration}}}$$

- As concentration increases $\Rightarrow \alpha$ decreases
- At infinite dilution α reaches its maximum value, unity.



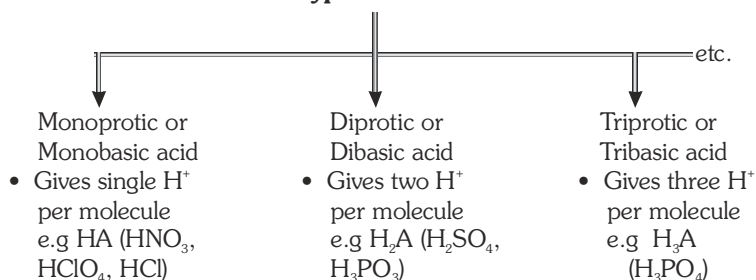
2. ACIDS BASES AND SALTS

2.1 Arrhenius concept :

- (i) **Arrhenius Acid** : Substance which gives H^+ ion on dissolving in water (H^+ donor)

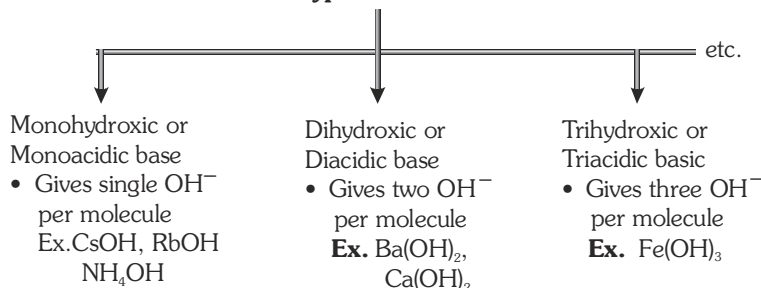
Ex. HNO_3 , $HClO_4$, HCl , HI , HBr , H_2SO_4 , H_3PO_4 etc.

Types of acids



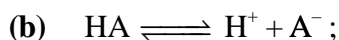
- (ii) **Arrhenius base** : Any substance which releases OH^- (hydroxyl) ion in water (OH^- ion donor)

Types of bases



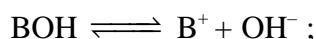
(iii) **Strength of Acid or Base :**

- (a) Strength of acids or bases depends on the extent of its ionisation. Hence equilibrium constant K_a or K_b respectively of the following equilibria give a quantitative measurement of the strength of the acid or base.



$$K_a = \frac{[H^+][A^-]}{[HA]} = \text{dissociation or ionisation constant of acid.}$$

- (c) Similarly

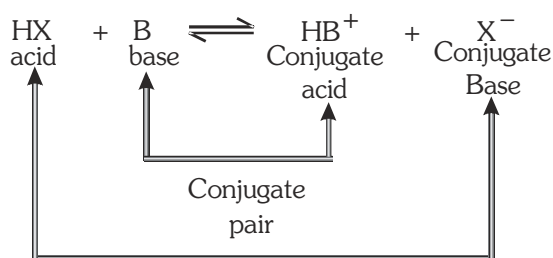


$$K_b = \frac{[B^+][OH^-]}{[BOH]} = \text{dissociation or ionisation constant of base}$$

- (d) Larger the value of K_a or K_b , stronger is the acid or base respectively.

2.2 **Bronsted - Lowry concept : (Conjugate acid - base concept) (Protonic concept)**

- (i) **Acid** : substances which donate H^+ are Bronsted Lowry acids (H^+ donor)
- (ii) **Base** : substances which accept H^+ are Bronsted Lowry bases (H^+ acceptor)
- (iii) **Conjugate acid - base pairs** : In a typical acid base reaction, $HX + B \rightleftharpoons X^- + HB^+$

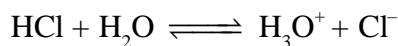


- Forward reaction - Here HX being a proton donor is an acid
B being a proton acceptor is a base.
- Backward reaction - Here HB^+ being a proton donor is an acid
 X^- being a proton acceptor is a base.

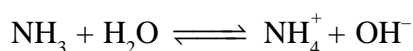
Acid	Base		Conjugate Acid		Conjugate Base
• HCl	+ H ₂ O	\rightleftharpoons	H ₃ O ⁺	+	Cl ⁻
• HSO ₄ ⁻	+ NH ₃	\rightleftharpoons	NH ₄ ⁺	+	SO ₄ ⁻²
• [Fe(H ₂ O) ₆] ³⁺	+ H ₂ O	\rightleftharpoons	H ₃ O ⁺	+	[Fe(H ₂ O) ₅ (OH)] ²⁺
• Conjugate acid - base pair differ by only one proton.					
• Strong acid will have weak conjugate base and vice versa.					

Acid	Conjugate base	Base	Conjugate acid
HCl	Cl^-	NH_3	NH_4^+
H_2SO_4	HSO_4^-	H_2O	H_3O^+
HSO_4^-	SO_4^{2-}	RNH_2	RNH_3^+
H_2O	OH^-		

(iv) **Amphoteric (amphiprotic)** : Substances which can act as acid as well as base are known as amphoteric



base



acid

(v) **Classification of Bronsted - Lowry Acids and Bases :**

Bronsted - Lowry acids and bases can be

- (i) Molecular (ii) Cationic and (iii) Anionic

Table - 1

Type	Acid	Base
Molecular	HCl, HNO_3 , HClO_4 , H_2SO_4 , H_3PO_4 , H_2O etc.	NH_3 , N_2H_4 , Amines, H_2O , Alcohol, Ethers, etc.
Cationic	NH_4^+ , N_2H_5^+ , PH_4^+ , $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ etc.	$[\text{Fe}(\text{H}_2\text{O})_5\text{OH}]^{2+}$ $[\text{Al}(\text{H}_2\text{O})_5\text{OH}]^{2+}$ etc.
Anionic	HS^- , HSO_3^- , H_2PO_4^- , HSO_4^- HCO_3^- , HPO_4^{2-} , etc. all amphiprotic anions	Cl^- , Br^- , OH^- , HSO_4^- , CN^- , CO_3^{2-} , SO_4^{2-} , NH_2^- , CH_3COO^- , etc. all amphiprotic anions

2.3 **Lewis concept (electronic concept) :**

- (i) **Acid** : An acid is a molecule/ion which can accept an electron pair with the formation of a coordinate bond.

Ex. Electron deficient molecules : BF_3 , AlCl_3 , etc.

Cations : H^+ , Fe^{2+} , Na^+ , etc.

Molecules with vacant orbitals : SF_4 , PF_3

- (ii) **Base** : A base is any molecule/ion which has a pair of electrons which can be donated.

Ex. Molecules with lone pairs : NH_3 , PH_3 , H_2O , CH_3OH

Anions : OH^- , H^- , NH_2^- , etc.

3. PROPERTIES OF WATER

(i) Molar concentration / Molarity of water :

$$\text{Molarity} = \text{No. of moles/litre} = \frac{1000 \text{ g/litre}}{18 \text{ g/mole}} = 55.55 \text{ mole/litre} = \mathbf{55.55 \text{ M}} \text{ (density} = 1 \text{ g/cc)}$$

(ii) Ionic product of water :

According to arrhenius concept, $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$

So, ionic product of water, $K_w = [\text{H}^+][\text{OH}^-] = 10^{-14}$ at 25° (experimental)

Dissociation of water is endothermic, so on increasing temperature K_w increases.

(iii) Degree of dissociation of water :

$$\begin{aligned} \text{H}_2\text{O} &\rightleftharpoons \text{H}^+ + \text{OH}^- \Rightarrow \alpha = \frac{\text{decrease in concentration}}{\text{initially concentration}} \\ &= \frac{10^{-7}}{55.55} = 18 \times 10^{-10} \text{ or } 1.8 \times 10^{-7} \% \quad [\text{at } 25^\circ\text{C}] \end{aligned}$$

(iv) Dissociation or ionisation constant of water :

$$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \quad K_a = K_b = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = \frac{10^{-7} \times 10^{-7}}{55.55} = 1.8 \times 10^{-16}$$

$$\text{So, } pK_a = pK_b = -\log(1.8 \times 10^{-16}) = 16 - \log 1.8 = 15.74$$

Ex.2. At dissociation constant of heavy water is 4×10^{-15} at 35°C . If its density is 1.04 g/mL . Calculate its ionic product & degree of dissociation.

$$\text{Sol. } K_w = K_d[D_2O] = \left(4 \times 10^{-15} \times \frac{1040}{20}\right) = 2.08 \times 10^{-13}$$

$$d = \sqrt{\frac{K_w}{C}} = \sqrt{\frac{2.08 \times 10^{-13}}{52}} = 12.64 \times 10^{-8}$$

Ex.3 Calculate ionic product of H_2O at 50°C .

$$\text{Sol. } \Delta H = 13.7 \times 10^3 \text{ cal}$$

$$\log \frac{K_2}{K_1} = \frac{\Delta H}{2} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Ex.4 The hydronium ion conc. in an aq. H_2CO_3 solution is $4 \times 10^{-4} \text{ M}$ at 25°C OH^- ion conc. in the solution is :

- (A) 0 (B) 2.5×10^{-10} (C) 2.5×10^3 (D) $2.5 \times 10^{-11} \text{ M}$

Answer : (D)

Ex.5 Select the correct option from the following ?

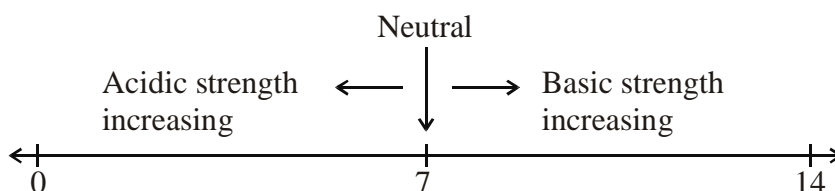
- (A) pK_w increases with increase of temperature
 (B) pK_w decreases with increase of temperature
 (C) $pK_w = 14$ at all temperatures
 (D) $pK_w = pH$ at all temperatures

Sol. (B)

4. Acidity and pH scale :

- (i) Acidic strength means the tendency of an acid to give H_3O^+ or H^+ ions in water.
So greater then tendency to give H^+ , more will be the acidic strength of the substance.
- (ii) Basic strength means the tendency of a base to give OH^- ions in water.
So greater the tendency to give OH^- ions, more will be basic strength of the substance.
- (iii) The concentration of H^+ ions is written in a simplified form introduced by **Sorenson** known as pH scale. pH is defined as negative logarithm of activity of H^+ ions.
 $\therefore \text{pH} = -\log a_{\text{H}^+}$ (where a_{H^+} is the activity of H^+ ions)
- (iv) Activity of H^+ ions is the molar concentration of free H^+ ions or H_3O^+ ions in a dilute solution, but unitless.
- (v) Now $\text{pH} = -\log[\text{H}^+] = 7$ and $\text{pOH} = -\log[\text{OH}^-] = 7$ for water at 25°C (experimental)

$$\left. \begin{array}{l} \text{pH} = 7 = \text{pOH} \Rightarrow \text{neutral} \\ \text{pH} < 7 \text{ or } \text{pOH} > 7 \Rightarrow \text{acidic} \\ \text{pH} > 7 \text{ or } \text{pOH} < 7 \Rightarrow \text{Basic} \end{array} \right\} \text{ at } 25^\circ\text{C}$$

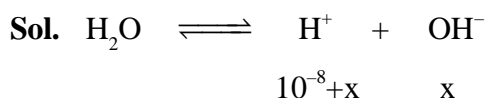


4.1 pH Calculation of different Types of solutions :

(a) Strong acid solution :

- (i) If concentration of H^+ ions is greater than 10^{-6}M , H^+ ions coming from water can be neglected,
So $[\text{H}^+] = \text{normality of strong acid solution}$
- (ii) If concentration is less than 10^{-6}M , H^+ ions coming from water cannot be neglected. So
 $[\text{H}^+] = \text{normality of strong acid} + \text{H}^+ \text{ ions coming from water in presence of this strong acid}$

Ex.6 Calculate pH of 10^{-8}M HCl solution.



$$K_w = [\text{H}^+][\text{OH}^-]$$

$$10^{-14} = x(x + 10^{-8})$$

$$\Rightarrow x^2 + x \times 10^{-8} - 10^{-14} = 0$$

$$x = \frac{-10^{-8} \pm \sqrt{10^{-16} + 4 \times 10^{-14}}}{2} = \frac{-10^{-8} + 10^{-7} \sqrt{4 + \frac{1}{100}}}{2} = \frac{(\sqrt{401} - 1)10^{-8}}{2} = 0.95 \times 10^{-7}$$

$$[\text{H}^+] = 10.5 \times 10^{-8} = 1.05 \times 10^{-7}$$

$$\text{pH} = -\log [\text{H}^+]$$

$$\text{pH} = 7 - \log 1.05 \approx 6.98$$

4.2 Strong base solution :

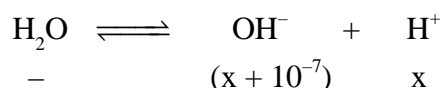
Calculate the $[\text{OH}^-]$ which will be equal to normality of the strong base solution and then use

$$K_w = [\text{H}^+] \times [\text{OH}^-] = 10^{-14}, \text{ to calculate } [\text{H}^+]$$

Ex.7 Calculate pH of 10^{-7} M of NaOH solution

Sol. $[\text{OH}^-]$ from NaOH = 10^{-7}

$[\text{OH}^-]$ from water = $x < 10^{-7} \text{ M}$ (due to common ion effect)



$$K_w = [\text{H}^+] [\text{OH}^-] = 10^{-14} = x (x + 10^{-7})$$

$$x^2 + 10^{-7}x - 10^{-14} = 0$$

$$\Rightarrow x = \frac{\sqrt{5}-1}{2} \times 10^{-7} = 0.618 \times 10^{-7} \quad (\sqrt{5} = 2.236)$$

$$[\text{OH}^-] = 10^{-7} + 0.618 \times 10^{-7} = 1.618 \times 10^{-7}$$

$$\text{pOH} = 7 - \log(1.618) = 6.79$$

$$\text{pH} = 14 - 6.79 = 7.21$$

4.3 pH of mixture of two strong acids : If V_1 volume of a strong acid solution of normality N_1 is mixed with V_2 volume of another strong acid solution of normality N_2 , then

$$\text{Number of } \text{H}^+ \text{ ions from I-solution} = N_1 V_1$$

$$\text{Number of } \text{H}^+ \text{ ions from II-solution} = N_2 V_2$$

If final normality is N and final volume is V , then

$$NV = N_1 V_1 + N_2 V_2$$

[dissociation equilibrium of none of these acids will be disturbed as both are strong acid]

$$[\text{H}^+] = N = \frac{N_1 V_1 + N_2 V_2}{V_1 + V_2} \quad \left[\begin{array}{l} \text{where } N = M \times n \\ n = \text{Basicity of acid} \end{array} \right]$$

4.4 pH of mixture of two strong bases :

Similar to above calculation

$$[\text{OH}^-] = N = \frac{N_1 V_1 + N_2 V_2}{V_1 + V_2} \quad [\text{H}^+] = \frac{10^{-14}}{[\text{OH}^-]}$$

$$\left[\begin{array}{l} \text{where } N = M \times n \\ n = \text{Acidity of base} \end{array} \right]$$

Ex.8 Calculate pH of mixture of $(400 \text{ mL}, \frac{1}{200} \text{ M H}_2\text{SO}_4) + (400 \text{ mL}, \frac{1}{100} \text{ M HCl}) + (200 \text{ mL of water})$

Sol. $N_1 V_1 = \frac{1}{200} \times \frac{400}{1000} \times 2 = \frac{4}{1000}$, $N_2 V_2 = \frac{4}{1000}$, H^+ ions from water will be neglected

$$N_1 V_1 + N_2 V_2 = 8 \times 10^{-3} \quad [\text{H}^+] = \frac{8 \times 10^{-3}}{1} = 8 \times 10^{-3}$$

$$\text{pH} = 3 - \log 8 = 2.1$$

Ex.9 500 mL of 10^{-5} M NaOH is mixed with 500 mL of 2.5×10^{-5} M of $\text{Ba}(\text{OH})_2$. To the resulting solution 99 L water is added. Calculate pH.

Sol. $[\text{OH}^-] = \frac{500 \times 10^{-5} + 500 \times 2 \times 2.5 \times 10^{-5}}{1000} = 3 \times 10^{-5} \text{ M}$

$$M_1 = 3 \times 10^{-5} \text{ M}$$

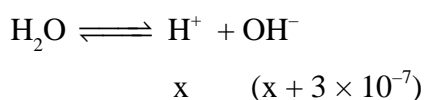
$$V_2 + V_1 = 1 \text{ L}$$

$$V_F = 100 \text{ L}$$

no. of moles of $[\text{OH}^-]$ initially = no. of moles of $[\text{OH}^-]$

$$3 \times 10^{-5} = M_2 \times 100$$

$$\therefore M_2 = 3 \times 10^{-7} < 10^{-6}$$



$$K_w = x(x + 3 \times 10^{-7}) = 10^{-14}$$

$$\therefore x = \left(\frac{\sqrt{13} - 3}{2} \right) \times 10^{-7}$$

$$x = 0.302 \times 10^{-7}$$

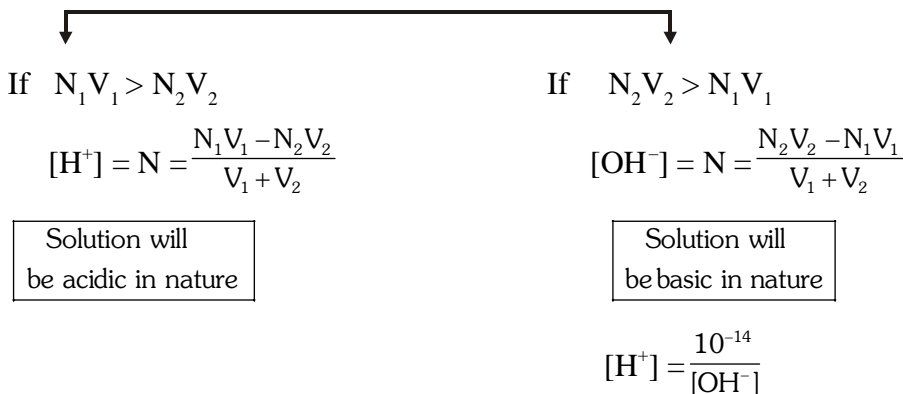
$$[\text{OH}^-]_{\text{Net}} = 3.302 \times 10^{-7}$$

4.5 pH of mixture of a strong acid and a strong base :

- Acid Base neutralisation reaction will take place.
- The solution will be acidic or basic depending on which component has been taken in excess.
- If V_1 volume of a strong acid solution of normality N_1 is mixed with V_2 volume of a strong base solution of normality N_2 , then

$$\text{Number of } \text{H}^+ \text{ ions from I-solution} = N_1 V_1$$

$$\text{Number of } \text{OH}^- \text{ ions from II-solution} = N_2 V_2$$



Ex.10 Calculate pH of mixture of (400 mL, $\frac{1}{200}$ M Ba(OH)₂) + (400 mL, $\frac{1}{50}$ M HCl) + (200 mL of water)

Sol. $[H^+] = \frac{400 \times \frac{1}{50} - 400 \times \frac{1}{200} \times 2}{1000} = 4 \times 10^{-3}$, so $pH = 3 - 2 \log 2 = 2.4$

Ex.11 What will be the resultant pH when 150 mL of an aqueous solution of HCl (pH = 2.0) is mixed with 350 mL of an aqueous solution of NaOH (pH = 12.0) ?

Sol. pH of HCl = 2

$\therefore [HCl] = 10^{-2}$ M

pH of NaOH = 12, $pOH = 2 \therefore [NaOH] = 10^{-2}$ M

	HCl	+	NaOH	→	NaCl	+	H ₂ O
Meq. initial	150×10^{-2}		350×10^{-2}		0		0
	= 1.5		= 3.5				
Meq. final	0		2		1.5		1.5

$\therefore [OH^-] \text{ from NaOH} = \frac{2}{500} = 4 \times 10^{-3}$ M

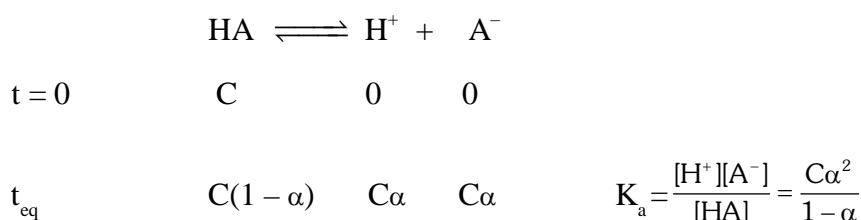
$pOH = -\log[OH^-] = -\log(4 \times 10^{-3})$

$\therefore pOH = 2.3979$

$\therefore pH = 14 - pOH = 14 - 2.3979 = 11.6021$

4.6 pH of a weak acid or weak base (monoprotic) Solution :

- Weak acid does not dissociated 100 % therefore we have to calculate the percentage dissociation using K_a dissociation constant of the acid.
- We have to use Ostwald's Dilution law (as have been derived earlier)



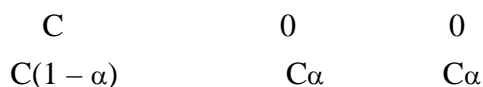
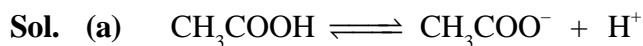
If $\alpha \ll 1 \Rightarrow (1 - \alpha) \approx 1 \Rightarrow K_a \approx C\alpha^2 \Rightarrow \alpha = \sqrt{\frac{K_a}{C}}$ (is valid if $\alpha < 0.1$ or 10%)

$[H^+] = C\alpha = C\sqrt{\frac{K_a}{C}} = \sqrt{K_a \times C}$ So $pH = \frac{1}{2}(pK_a - \log C)$

On increasing the dilution $\Rightarrow C \downarrow = \alpha \uparrow$ and $[H^+] \downarrow \Rightarrow pH \uparrow$

Ex.12 Calculate pH of : (a) 10^{-1} M CH_3COOH (b) 10^{-3} M CH_3COOH (c) 10^{-6} M CH_3COOH

Take $K_a = 2 \times 10^{-5}$



$$K_a = \frac{\text{C}\alpha^2}{1-\alpha} \Rightarrow \alpha = \sqrt{\frac{K_a}{\text{C}}} = \sqrt{\frac{2 \times 10^{-5}}{10^{-1}}} = \sqrt{2 \times 10^{-4}} \quad (\alpha \ll 0.1)$$

$$\text{So, } [\text{H}^+] = 10^{-1} \times \sqrt{2} \times 10^{-2} \Rightarrow \text{pH} = 3 - \frac{1}{2} \log 2 = 2.85$$

(b) $\alpha = \sqrt{\frac{K_a}{\text{C}}} \Rightarrow \alpha = \sqrt{\frac{K_a}{\text{C}}} = \sqrt{\frac{2 \times 10^{-5}}{10^{-3}}} = \sqrt{2 \times 10^{-2}} \quad (\alpha > 0.1)$

So we have to do the exact calculations

$$K_a = \frac{\text{C}\alpha^2}{1-\alpha} \Rightarrow 2 \times 10^{-5} = \frac{10^{-3} \times \alpha^2}{1-\alpha} \Rightarrow \alpha = 13.14 \%$$

$$[\text{H}^+] = 10^{-3} \times 0.1314 = 1.314 \times 10^{-4} \Rightarrow \text{pH} = 4 - \log(1.314) \approx 3.8$$

(c) If approximation is used the, $\alpha = \sqrt{\frac{2 \times 10^{-5}}{10^{-6}}} = \sqrt{20} > 1$,

So we have to do the exact calculation, $2 \times 10^{-5} = 10^{-6} \frac{\alpha^2}{1-\alpha} \Rightarrow \alpha \approx 0.95$ or 95%

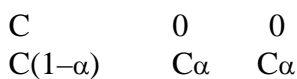
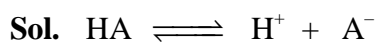
$$[\text{H}^+] = 0.95 \times 10^{-6} = 9.5 \times 10^{-7} \Rightarrow \text{pH} = 7 - \log(9.5) = 6.022$$

- At very low concentration (at infinite dilution) weak electrolyte will be almost 100% dissociate, so behave as strong electrolyte.

(pH) of 10^{-6} M HCl \approx pH of 10^{-6} M $\text{CH}_3\text{COOH} \approx 6$

Ex.13 K_a for acid HA is 2.5×10^{-8} calculate for its decimolar solution at 25°C .

(i) % dissociation (ii) pH (iii) OH^- ion concentration



$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \Rightarrow K_a = \frac{\text{C}\alpha \cdot \text{C}\alpha}{\text{C}(1-\alpha)} = \frac{\text{C}\alpha^2}{(1-\alpha)} \approx \text{C}\alpha^2$$

(i) $\therefore \alpha = \sqrt{\frac{K_a}{\text{C}}} = \sqrt{\frac{2.5 \times 10^{-8}}{1/10}} \quad (\text{C} = 1/10 \text{ M})$
 $= 5 \times 10^{-4} = 0.05\%$

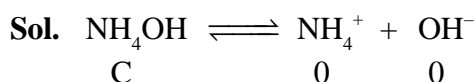
(ii) $[\text{H}^+] = \text{C}\alpha = \frac{1}{10} \times 5 \times 10^{-4} = 5 \times 10^{-5} \text{ mol/L}$

So $\text{pH} = 5 - \log 5 = 4.30$

(iii) $[\text{H}^+][\text{OH}^-] = 1 \times 10^{-14}$

$$\therefore [\text{OH}^-] = \frac{10^{-14}}{5 \times 10^{-5}} = 2 \times 10^{-10} \text{ mol/L}$$

Ex.14 Determine the degree of dissociation of $0.05\text{ M NH}_4\text{OH}$ at 25°C in a solution of $\text{pH} = 10$.



Given, $\text{pH} = 10$

$$[\text{H}^+] = 10^{-10}$$

$$[\text{H}^+][\text{OH}^-] = 1 \times 10^{-14}$$

$$\therefore [\text{OH}^-] = \frac{1 \times 10^{-14}}{10^{-10}} = 10^{-4} = C\alpha$$

$$\therefore \alpha = \frac{[\text{OH}^-]}{C} = \frac{10^{-4}}{0.05} = 2 \times 10^{-3} \text{ or } 0.2\%$$

Ex.15 The concentration of $[\text{H}^+]$ and $[\text{OH}^-]$ of the 10^{-1} M aqueous solution of 2% ionised weak acid is :

(A) $2 \times 10^{-3}\text{ M}$ and $5 \times 10^{-12}\text{ M}$

(B) $1 \times 10^{-3}\text{ M}$ and $3 \times 10^{-11}\text{ M}$

(C) $2 \times 10^{-4}\text{ M}$ and $5 \times 10^{-11}\text{ M}$

(D) $3 \times 10^{-2}\text{ M}$ and $4 \times 10^{-13}\text{ M}$

Sol. (A)

$$[\text{H}^+] = C\alpha = 2 \times 10^{-3}\text{ M} \text{ or } [\text{OH}^-] = \frac{10^{-14}}{[\text{H}^+]} = 5 \times 10^{-12}\text{ M}$$

Ex.16 When a 0.1 N solution of an acid at 25°C has a degree of ionisation of 4%, the concentration of OH^- present is :

(A) 2.5×10^{-3}

(B) 2.5×10^{-11}

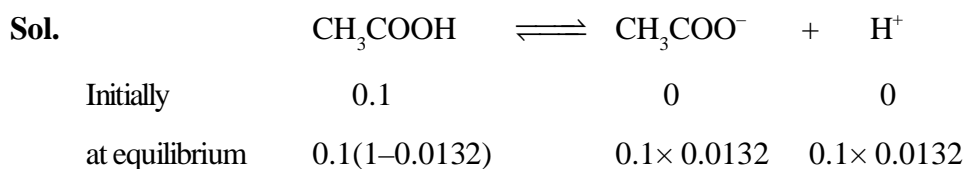
(C) 2.5×10^{-12}

(D) 2.5×10^{-13}

Sol. (C)

$$[\text{H}^+] = C\alpha = 0.1 \times 4 \times 10^{-2} = 4 \times 10^{-3}\text{ M} \text{ or } [\text{OH}^-] = \frac{10^{-14}}{[\text{H}^+]} = 2.5 \times 10^{-12}\text{ N}$$

Ex.17 The degree of dissociation of acetic acid in a 0.1 M solution is 1.32×10^{-2} . Calculate dissociation constant of acid and its pK_a value :

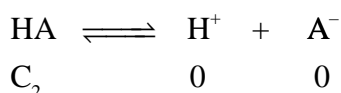


$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = \frac{0.1 \times 0.0132 \times 0.1 \times 0.0132}{0.1(1 - 0.0132)} = 1.76 \times 10^{-5}$$

$$\text{pK}_a = -\log K_a = -\log (1.76 \times 10^{-5}) = 4.75$$

4.7 pH of a mixture of weak acid (monoprotic) and a strong acid solution :

- Weak acid and Strong acid both will contribute H^+ ion.
- For the first approximation we can neglect the H^+ ions coming from the weak acid solution and calculate the pH of the solution from the concentration of the strong acid only.
- To calculate exact pH, we have to take the effect of presence of strong acid on the dissociation equilibrium of the weak acid.
- If $[SA] = C_1$ and $[WA] = C_2$, then $[H^+]$ from $SA = C_1$ the weak acid will dissociate as follows.



$$\begin{array}{ccccc} C_2(1 - \alpha) & C_2\alpha + C_1 & C_2\alpha & & K_a = \frac{(C_2\alpha + C_1)C_2\alpha}{C_2(1 - \alpha)} \quad (\alpha \ll 1) \end{array}$$

(The weak acids dissociation will be further suppressed because of presence of strong acid, common ion effect)

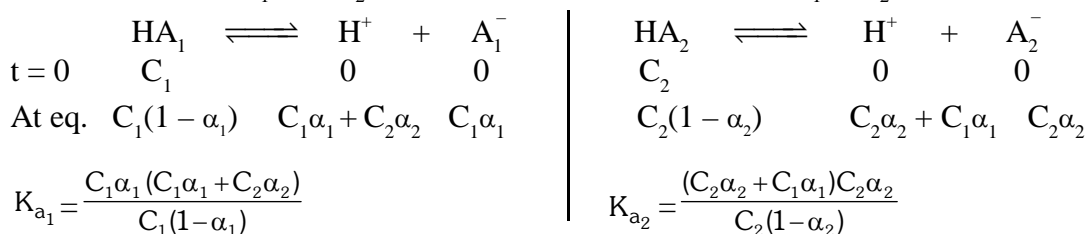
$$K_a = (C_2\alpha + C_1)\alpha$$

Total H^+ ion concentration = $C_1 + C_2\alpha$

- If the total $[H^+]$ from the acid is more than $10^{-6} M$, then contribution from the water can be neglected, if not then we have to take $[H^+]$ from the water also.

4.8 pH of a mixture of two weak acid (both monoprotic) solution :

- Both acids will dissociate partially.
- Let the acid are HA_1 & HA_2 and their final concentrations are C_1 & C_2 respectively, then



(Since α_1, α_2 both are small in comparison to unity)

$$K_{a1} = (C_1\alpha_1 + C_2\alpha_2)\alpha_1 ; K_{a2} = (C_1\alpha_1 + C_2\alpha_2)\alpha_2 \Rightarrow \frac{K_{a1}}{K_{a2}} = \frac{\alpha_1}{\alpha_2}$$

$$\begin{aligned} [H^+] = C_1\alpha_1 + C_2\alpha_2 &= \frac{C_1K_{a1}}{\sqrt{C_1K_{a1} + C_2K_{a2}}} + \frac{C_2K_{a2}}{\sqrt{C_1K_{a1} + C_2K_{a2}}} \Rightarrow [H^+] \\ &= \sqrt{C_1K_{a1} + C_2K_{a2}} \end{aligned}$$

- If the dissociation constant of one of the acid is very much greater than that of the second acid then contribution from the second acid can be neglected.

$$\text{So, } [H^+] = C_1\alpha_1 + C_2\alpha_2 \approx C_1\alpha_1$$

Ex.18 Calculate pH of solution obtained by mixing equal vol. of 0.02 M HOCl & 0.2 M CH₃COOH solution given that $K_{a_1}(\text{HOCl}) = 2 \times 10^{-4}$, $K_{a_2}(\text{CH}_3\text{COOH}) = 2 \times 10^{-5}$

Also calculate OH⁻, OCl⁻, CH₃COO⁻

Sol. Final solution volume become double

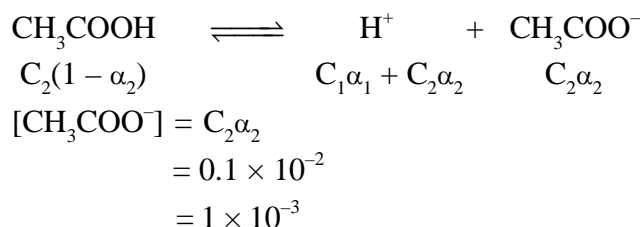
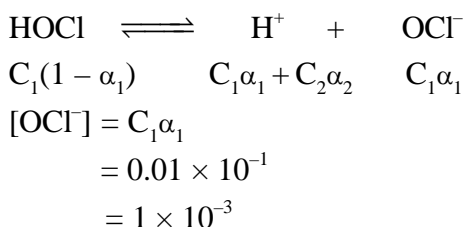
$$C_1 = 0.01, \quad C_2 = 0.1$$

$$[\text{H}^+] = \sqrt{K_{a_1}C_1 + K_{a_2}C_2} = \sqrt{2 \times 10^{-4} \times 0.01 + 2 \times 10^{-5} \times 0.1}$$

$$= \sqrt{2 \times 10^{-6} + 2 \times 10^{-6}} = 2 \times 10^{-3}$$

$$\text{pH} = 3 - \log 2 = 3 - 0.3010 = 2.69$$

$$\alpha_1 = \frac{2 \times 10^{-4}}{2 \times 10^{-3}} = 10^{-1} \quad \alpha_2 = \frac{2 \times 10^{-5}}{2 \times 10^{-3}} = 10^{-2}$$



$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{10^{-14}}{2 \times 10^{-3}} = 0.5 \times 10^{-11} = 5 \times 10^{-12} \text{ M}$$

$$[\text{HOCl}] = 10^{-2}(1 - 0.1) = 9 \times 10^{-3} \text{ M}$$

$$[\text{CH}_3\text{COOH}] = 10^{-1}(1 - 0.01) \approx 10^{-1}$$

4.9 pH of a solution of a polyprotic weak acid :

- Diprotic acid is the one, which is capable of giving 2 protons per molecule in water. Let us take a weak diprotic acid (H₂A) in water whose concentration is c M.

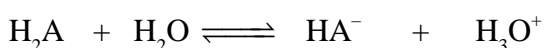
In an aqueous solution, following equilibria exist.

If

α_1 = degree of ionization of H₂A in presence of HA⁻ K_{a_1} = first ionisation constant of H₂A

α_2 = degree of ionisation of HA⁻ in presence of H₂A K_{a_2} = second ionisation constant of H₂A

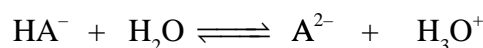
I step



at eq. $c(1 - \alpha_1)$ $c\alpha_1(1 - \alpha_2)$ $(c\alpha_1 + c\alpha_1\alpha_2)$

$$(K_{\text{eq}})_1 [\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{HA}^-]}{[\text{H}_2\text{A}]} = K_{a_1}$$

II step



at eq. $c\alpha_1(1 - \alpha_2)$ $c\alpha_1\alpha_2$ $(c\alpha_1 + c\alpha_1\alpha_2)$

$$(K_{\text{eq}})_2 [\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{A}^{2-}]}{[\text{HA}^-]} = K_{a_2}$$

$$\therefore K_{a_1} = \frac{(c\alpha_1 + c\alpha_1\alpha_2)[c\alpha_1(1-\alpha_2)]}{c(1-\alpha_1)} \quad K_{a_2} = \frac{(c\alpha_1 + c\alpha_1\alpha_2)[c\alpha_1\alpha_2]}{c\alpha_1(1-\alpha_2)}$$

$$= \frac{[c\alpha_1(1+\alpha_2)][\alpha_1(1-\alpha_2)]}{1-\alpha_1} \dots\dots (i) \quad = \frac{[c\alpha_1(1+\alpha_2)]\alpha_2}{1-\alpha_2} \dots\dots (ii)$$

Knowing the values of K_{a_1} , K_{a_2} and c , the values of α_1 and α_2 can be calculated using equations (i)

and (ii) After getting the values of α_1 and α_2 , $[H_3O^+]$ can be calculated as

$$[H_3O^+]_T = c\alpha_1 + c\alpha_1\alpha_2$$

Finally, for calculation of pH

- If the total $[H_3O^+] < 10^{-6} M$, the contribution of H_3O^+ from water should be added.
- If the total $[H_3O^+] > 10^{-6} M$, then $[H_3O^+]$ contribution from water can be ignored.

Using this $[H_3O^+]$, pH of the solution can be calculated.

❖ Approximation :

For diprotic acids, $K_{a_2} \ll K_{a_1}$ and α_2 would be even smaller than α_1

$$\therefore 1 - \alpha_2 \approx 1 \text{ and } 1 + \alpha_2 \approx 1$$

Thus, equation (i) can be reduced to $K_{a_1} = \frac{C\alpha_1 \times \alpha_1}{1 - \alpha_1}$

This is expression similar to the expression for a weak monoprotic acid.

- Hence, for a diprotic acid (or a polyprotic acid) the $[H_3O^+]$ can be calculated from its first equilibrium constant expression alone provided $K_{a_2} \ll K_{a_1}$.

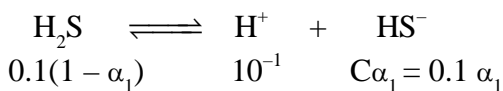
Ex.19 Calculate pH of $[HS^-]$, $[S^{2-}]$, $[Cl^-]$ in a solution which is 0.1 M HCl & 0.1 M H_2S given that $K_{a_1}(H_2S) = 10^{-7}$, $K_{a_2}(H_2S) = 10^{-14}$ also calculate α_1 & α_2 .

Sol. $HCl + H_2S$

$$0.1 \quad 0.1$$

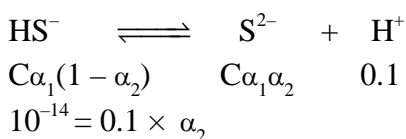
$$C_1 = C_2 = 0.1$$

$$\therefore pH = 1 \quad (\text{most of } [H^+] \text{ comes from HCl})$$



$$K_{a_1} = \frac{C\alpha_1 \times 10^{-1}}{C(1 - \alpha_1)} = \frac{10^{-7}}{10^{-1}} = \alpha_1 \quad (\because 1 - \alpha_1 = 1)$$

$$\Rightarrow \alpha_1 = 10^{-6}$$



$$\Rightarrow \alpha_2 = 10^{-13}$$

$$[S^{2-}] = C\alpha_1\alpha_2$$

$$= 10^{-6} \times 10^{-1} \times 10^{-13} = 10^{-20} M$$

4.10 ISOHYDRIC SOLUTIONS

- (i) Solutions of electrolytes are said to be isohydric if the concentration of the common ion present in them is the same and on mixing such solutions, there occurs no change in the degree of dissociation of either of the electrolyte.
- (ii) Let the isohydric solution is made by HA_1 and HA_2 acids, then $[H^+]$ of both acids should be equal i.e.

$$\sqrt{K_{a_1} C_1} = \sqrt{K_{a_2} C_2} \quad \text{or} \quad \frac{K_{a_1}}{K_{a_2}} = \frac{C_2}{C_1}$$

4.11 RELATIVE STRENGTH OF WEAK ACIDS AND BASES

For two acids of equimolar concentrations.

$$\frac{\text{Strength of acid (I)}}{\text{Strength of acid (II)}} = \sqrt{\frac{K_{a_1}}{K_{a_2}}}$$

Similarly for bases,
$$\frac{\text{Strength of base (I)}}{\text{Strength of base (II)}} = \sqrt{\frac{K_{b_1}}{K_{b_2}}}$$

The modern method is to convert K_a as a power of 10 and express acid strength by power of 10 with sign changed and call this new unit pK_a . Thus, if K_a for acid is equal to 10^{-4} , $pK_a = 4$. So higher pK_a value means lower acid strength, that is, $pK_a = -\log K_a$

Also, $pK_b = -\log K_b$

5. SALTS

- (i) Salts are the ionic compounds formed when its positive part (Cation) come from a base and its negative part (Anion) come from an acid.
- (ii) Salts may taste salty, bitter or sweet or tasteless.
- (iii) Solution of salts may be acidic, basic or neutral.
- (iv) Fused salts and their aqueous solutions conduct electricity and undergo electrolysis.
- (v) The salts are generally crystalline solids.

5.1 Classification of salts :

The salts may be classified into four categories.

(a) Normal salt :

- (i) The salt formed by the loss of all possible protons (replaceable H^+ ions)

Ex. $NaCl$, $NaNO_3$, K_2SO_4 , $Ca_3(PO_4)_2$, Na_3BO_3 , Na_2HPO_3 , NaH_2PO_2 etc.

(b) Acid salts :

- (i) Salts formed by incomplete neutralisation of polybasic acids. Such salts contain one or more replaceable H atom.

Ex. $NaHCO_3$, $NaHSO_4$, NaH_2PO_4 , Na_2HPO_4 etc.

- (ii) Above salts when neutralized by base form normal salts.

(c) **Basic salts :**

- (i) Salts formed by in complete neutralisation of poly acidic bases are called basic salts. These salt contain one or more hydroxyl groups.

Ex. Zn(OH)Cl , Mg(OH)Cl , $\text{Fe(OH)}_2\text{Cl}$, $\text{Bi(OH)}_2\text{Cl}$ etc.

- (ii) Above salts when neutralised by acids form normal salts.

5.2 HYDROLYSIS OF SALTS

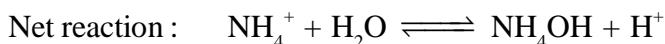
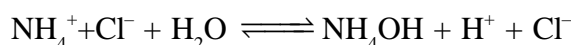
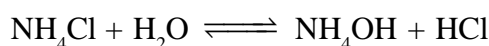
Salt hydrolysis is defined as the process in which water reacts with cation or anion or both of a salt to change the concentration of H^+ and OH^- ions of water.

Salt hydrolysis is reverse process of neutralization.

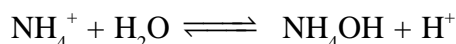


5.2.1 Hydrolysis of strong acid - weak base [SA - WB] type salt –

Ex. CaSO_4 , NH_4Cl , $(\text{NH}_4)_2\text{SO}_4$, $\text{Ca(NO}_3)_2$, ZnCl_2 , CuCl_2 , CaCl_2



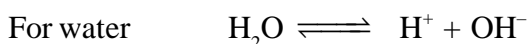
- (i) In this type of salt hydrolysis, cation reacts with H_2O , therefore called as **cationic hydrolysis**.
 (ii) Solution is acidic in nature (SAWB) as $[\text{H}^+]$ is increased.
 (iii) pH of the solution is less than 7.
 (iv) **Relation between K_h , K_w & K_b**



$$\text{Hydrolysis constant } K_h = \frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+]} \quad \dots\dots(i)$$



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} \quad \dots\dots(ii)$$



$$K_w = [\text{OH}^-][\text{H}^+] \quad \dots\dots(iii)$$

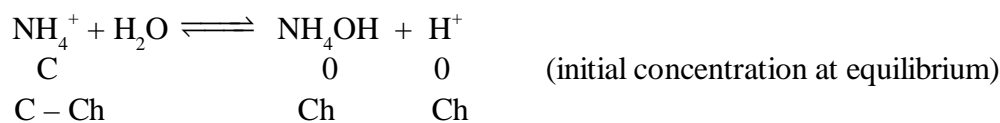
Now multiplying Eq. (1) & (2) = Eq. (3)

$$\frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+]} \times \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} = [\text{H}^+][\text{OH}^-]$$

$$\text{i.e. } K_h \times K_b = K_w$$

$$\boxed{K_h = \frac{K_w}{K_b}}$$

(v) Degree of hydrolysis – (Represented by h)



$$K_h = \frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+]} = \frac{\text{Ch}^2}{(1-h)}$$

Since $h \ll 1$ then $(1-h) \approx 1$

$$\therefore K_h = \text{Ch}^2$$

$$\Rightarrow h = \sqrt{\frac{K_h}{C}}$$

$$\therefore \Rightarrow h = \sqrt{\frac{K_w}{K_b C}} \Rightarrow \boxed{h = \sqrt{\frac{K_w}{K_b \times C}}}$$

(vi) pH of the solution :

$$\text{pH} = -\log [\text{H}^+]$$

$$\Rightarrow [\text{H}^+] = \sqrt{\frac{K_w \times C}{K_b}}$$

On taking $-\log$ on both sides

$$\text{pH} = -\log \left(\frac{K_w \times C}{K_b} \right)^{1/2}$$

$$\text{pH} = -\frac{1}{2} \log K_w - \frac{1}{2} \log C - \frac{1}{2} (-\log K_b)$$

$$\text{pH} = 7 - \frac{1}{2} \text{p}K_b - \frac{1}{2} \log C$$

Ex.20 Find out the K_h of centi normal $[10^{-2} \text{ N}]$ solution of NH_4Cl (SA - WB) if dissociation constant of NH_4OH is 10^{-6} and $K_w = 10^{-14}$. Find out degree of hydrolysis and also find $[\text{H}^+]$ and pH of solution?

(Given : $K_w = 10^{-14}$; $K_b = 10^{-6}$)

Sol. (1) $K_h = \frac{K_w}{K_b} = \frac{10^{-14}}{10^{-6}} = 10^{-8}$

(2) $h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{10^{-8}}{10^{-2}}} = \sqrt{10^{-6}} = 10^{-3}$

(3) $[\text{H}^+] = \text{Ch}$
 $= 10^{-2} \times 10^{-3} = 10^{-5}$

(4) $\text{pH} = -\log [\text{H}^+] = -\log [10^{-5}] = +5 \log 10 = +5 \times 1 = 5$

Ex.21 How many grams of NH_4Cl should be dissolved per litre of solution to have a pH of 5.13 ? K_b for NH_3 is 1.8×10^{-5} .

Sol. NH_4Cl is a salt of strong acid and weak base for solutions of such salts.

$$\text{pH} = \frac{1}{2} [\text{p}K_w - \log C - \text{p}K_b]$$

$$\Rightarrow 10.26 = 14 - \log C - 4.74$$

$$\Rightarrow \log C = 9.26 - 10.26 = -1.0$$

$$\therefore C = 10^{-1} \text{ M}$$

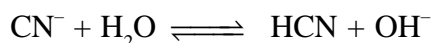
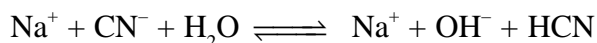
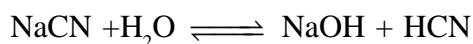
$$[\text{NH}_4\text{Cl}] = 10^{-1} \text{ M}$$

$$W_{\text{NH}_4\text{NO}_3} = 10^{-1} \times 53.5 \text{ gL}^{-1}$$

$$= 5.35 \text{ gL}^{-1}$$

5.2.2 Hydrolysis of [WA – SB] type salt :

Ex. KCN, NaCN, K_2CO_3 , BaCO_3 , K_3PO_4

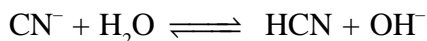


(i) In this type of salt hydrolysis anion reacts with water therefore called as anionic hydrolysis.

(ii) Solution is basic in nature as $[\text{OH}^-]$ increases.

(iii) pH of the solution is greater than 7.

(iv) **Relation between K_h , K_w , K_a**

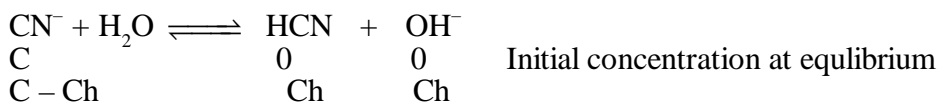


$$K_h = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]} \quad \dots (i)$$

$$\frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]} \times \frac{[\text{CN}^-][\text{H}^+]}{[\text{HCN}]} = [\text{H}^+][\text{OH}^-]$$

$$\boxed{K_h = \frac{K_w}{K_a}}$$

(v) **Degree of hydrolysis :**



$$K_h = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]}$$

$$K_h = \frac{\text{Ch}^2}{(1 - h)}$$

Since $h \ll 1$, therefore $(1 - h) \approx 1$

$$\therefore K_h = \text{Ch}^2$$

$$h^2 = \frac{K_h}{C}$$

$$\Rightarrow \boxed{h = \sqrt{\frac{K_h}{C}}}$$

$$\boxed{h = \sqrt{\frac{K_w}{K_a \times C}}}$$

(vi) pH of the solution

$$[\text{OH}^-] = \text{Ch}$$

$$[\text{OH}^-] = \sqrt{\frac{K_w \times C}{K_a}}$$

$$[\text{H}^+] = \frac{K_w}{\sqrt{\frac{K_w \times C}{K_a}}} \Rightarrow [\text{H}^+] = \sqrt{\frac{K_w \times K_a}{C}}$$

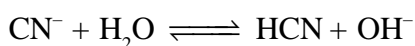
On taking -log on both sides

$$\text{pH} = -\frac{1}{2} [\log K_w + \log K_a - \log C]$$

$$\text{pH} = 7 + \frac{1}{2} \text{p}K_a + \frac{1}{2} \log C$$

Ex.22 Calculate the pH and degree of hydrolysis of 0.01 M solution of NaCN, K_a for HCN is 6.2×10^{-12} .

Sol. NaCN is a salt of strong base NaOH and weak acid HCN. Na^+ does not react with water whereas CN^- reacts with water as here under



$$K_h = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]} = \frac{K_w}{K_a} = \frac{10^{-14}}{6.2 \times 10^{-12}} = 1.6 \times 10^{-3}$$

Let, x moles of salt undergo hydrolysis then concentrations of various species would be

$$[\text{CN}^-] = (0.01 - x) \approx 0.01, [\text{HCN}] = x$$

$$[\text{OH}^-] = x$$

$$\therefore K_h = \frac{x \cdot x}{0.01} = 1.6 \times 10^{-3}$$

$$\therefore x^2 = 1.6 \times 10^{-5}$$

$$\therefore x = 4 \times 10^{-3}$$

$$[\text{OH}^-] = x = 4 \times 10^{-3} \text{ M}$$

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{10^{-14}}{4 \times 10^{-3}} = 0.25 \times 10^{-11}$$

$$\text{pH} = -\log(0.25 \times 10^{-11}) = 11.6020$$

$$\text{Degree of hydrolysis} = \frac{x}{0.01} = \frac{4 \times 10^{-3}}{0.01} = 4 \times 10^{-1}$$

Ex.23. Calculate for 0.01 N solution of sodium acetate -

- (i) Hydrolysis constant
- (ii) Degree of hydrolysis
- (iii) pH

Given K_a of $\text{CH}_3\text{COOH} = 1.9 \times 10^{-5}$.

Sol. For $\text{CH}_3\text{COONa} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{NaOH}$

Initial	C	0	0
After	$C(1-h)$	Ch	Ch

$$(i) \quad K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{1.9 \times 10^{-5}} = 5.26 \times 10^{-10}$$

$$(ii) \quad h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{5.26 \times 10^{-10}}{0.01}} = 2.29 \times 10^{-4} \text{ M}$$

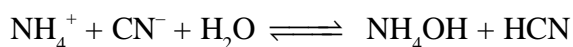
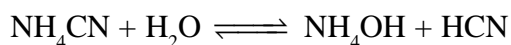
$$(iii) \quad [\text{OH}^-] \text{ from NaOH, a strong base} = \text{Ch} = 0.01 \times 2.29 \times 10^{-4} = 2.29 \times 10^{-6} \text{ M}$$

$$\text{pOH} = 5.64$$

$$\therefore \text{pH} = 14 - 5.64 = 8.36$$

5.2.3 Hydrolysis of (WA - WB) type salt :

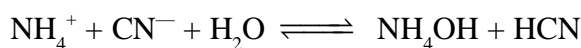
Ex. NH_4CN , CaCO_3 , $(\text{NH}_4)_2\text{CO}_3$, ZnHPO_3



Solution is almost neutral but it may be acidic or basic depending upon the nature of acid & base & pH of the solution is near to 7.

For WA - WB types of salt :

	$K_a > K_b$	$K_b > K_a$	$K_a = K_b$
1. Hydrolysis	Cationic-anionic	Anionic-cationic	Neutral hydrolysis
2. Nature	Acidic	Basic	Neutral
3. pH	$\text{pH} < 7$	$\text{pH} > 7$	$\text{pH} = 7$

(i) Relation between K_h , K_w , K_a & K_b 

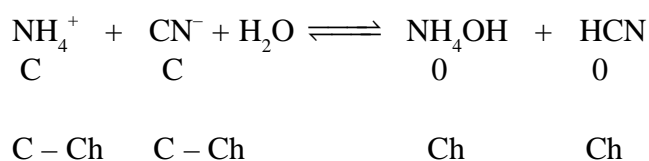
$$K_h = \frac{[\text{NH}_4\text{OH}][\text{HCN}]}{[\text{NH}_4^+][\text{CN}^-]} \quad \dots (i)$$

$$\frac{[\text{NH}_4\text{OH}][\text{HCN}]}{[\text{NH}_4^+][\text{CN}^-]} \times \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} \times \frac{[\text{H}^+][\text{CN}^-]}{[\text{HCN}]} = [\text{H}^+][\text{OH}^-]$$

$$K_h \times K_b \times K_a = K_w$$

$$\boxed{K_h = \frac{K_w}{K_a \times K_b}}$$

(ii) Degree of Hydrolysis :



Initial concentration
at equilibrium

$$K_h = \frac{[\text{NH}_4\text{OH}][\text{HCN}]}{[\text{NH}_4^+][\text{CN}^-]}$$

Since $h \ll \ll \ll 1$

Then $(1 - h) \approx 1$

$$\therefore \boxed{K_h = h^2} \quad \text{or} \quad h^2 = \frac{K_w}{K_a \times K_b}$$

$$h = \sqrt{\frac{K_w}{K_a \times K_b}} \quad \dots (v)$$

(iii) pH of the solution

From eq. (iii)

$$K_a = \frac{[\text{H}^+][\text{CN}^-]}{[\text{HCN}]}$$

$$[\text{H}^+] = \frac{K_a \times [\text{HCN}]}{[\text{CN}^-]}$$

$$[\text{H}^+] = \frac{K_a \times \text{Ch}}{\text{C} - \text{Ch}} = \frac{K_a \times h}{1 - h}$$

Since $h \ll \ll \ll 1$, $(1 - h) \approx 1$

$$[\text{H}^+] = K_a \times h \quad [\text{Now put the value of } h \text{ from eq. (5)}]$$

$$= K_a \times \sqrt{\frac{K_w}{K_a \times K_b}}$$

$$\boxed{[\text{H}^+] = \sqrt{\frac{K_w \times K_a}{K_b}}}$$

On taking $-\log$ on both sides

$$-\log [H^+] = -\log \left(\frac{K_w \times K_a}{K_b} \right)^{1/2}$$

$$pH = -\frac{1}{2} [\log K_w + \log K_a - \log K_b]$$

$$pH = 7 + \frac{1}{2} pK_a - \frac{1}{2} pK_b$$

Note : Degree of hydrolysis of [WA – WB] type salt does not depend on the concentration of salt.

Ex.24 Salt of weak acid and weak base

(i) Calculate pH of the mixture (25 mL of 0.1 M NH_4OH + 25 mL of 0.1 M CH_3COOH).

Given that $K_a : 1.8 \times 10^{-5}$, and $K_b = 1.8 \times 10^{-5}$

Sol.	NH_4OH	+	CH_3COOH	\rightarrow	CH_3COONH_4	+	H_2O
Initial milli moles	25×0.1		25×0.1		0		0
	= 2.5		= 2.5		–		
Final milli moles	0		0		2.5		2.5

As salt is formed (salt of weak acid and weak base) and pH will be decided by salt hydrolysis

$$pH = \frac{pK_w + pK_a - pK_b}{2} = \frac{1}{2} (-\log 10^{-14} - \log 1.8 \times 10^{-5} + \log 1.8 \times 10^{-5}) = 7$$

Ex.25 In the following which one has highest / maximum degree of hydrolysis.

(1) 0.01 M – NH_4Cl

(2) 0.1 M – NH_4Cl

(3) 0.001 M – NH_4Cl

(4) Same

Sol. [3]

$$\left(h = \sqrt{\frac{K_h}{C}} \quad \text{if } C \text{ decreases, } h \text{ increases} \right)$$

Ex.26 In the following which one has lowest value of degree of hydrolysis.

(1) 0.01 M – CH_3COONH_4

(2) 0.1 M – CH_3COONH_4

(3) 0.001 M – CH_3COONH_4

(4) Same

Sol. [4]

Ex.27 Find out the concentration of $[H^+]$ in 0.1M CH_3COONa solution ($K_a = 10^{-5}$)

Sol. Salt is [WA – SB] type

$$\therefore [H^+] = \sqrt{\frac{K_w \times K_a}{C}} = \sqrt{\frac{10^{-14} \times 10^{-5}}{10^{-1}}} = \sqrt{10^{-19} \times 10^{+1}} = \sqrt{10^{-18}} = 10^{-9}$$

Ex.28 Calculate the degree of hydrolysis of a mixture containing 0.1N NH_4OH and 0.1N HCN

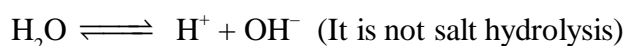
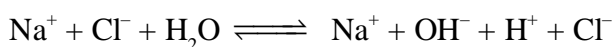
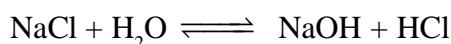
$$K_a = 10^{-5} \quad \& \quad K_b = 10^{-5}$$

Sol. Salt is [WA – WB]

$$h = \sqrt{\frac{K_w}{K_a \times K_b}} = \sqrt{\frac{10^{-14}}{10^{-5} \times 10^{-5}}} \\ = \sqrt{10^{-14} \times 10^{+10}} = \sqrt{10^{-4}} = 10^{-2}$$

5.2.4 Hydrolysis of [SA – SB] type salt :

Ex. NaCl , BaCl_2 , Na_2SO_4 , KClO_4 etc.



- (1) Hydrolysis of salt of [SA – SB] is not possible
- (2) Solution is neutral in nature ($\text{pH} = \text{pOH} = 7$)
- (3) pH of the solution is 7

5.2.5 Hydrolysis of Amphotropic Anion :

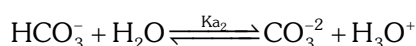
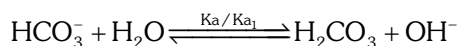
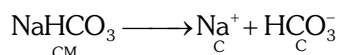
NaHCO_3 , NaHS , etc., can undergo ionisation to form H^+ ion and can undergo hydrolysis to form OH^- (Na^+ ion is not hydrolysed)

- (a) (i) $\text{HCO}_3^- + \text{H}_2\text{O} \xrightleftharpoons{\text{ionisation}} \text{CO}_3^{2-} + \text{H}_3\text{O}^+$ (acid)
- (ii) $\text{HCO}_3^- + \text{H}_2\text{O} \xrightleftharpoons{\text{hydrolysis}} \text{H}_2\text{CO}_3 + \text{OH}^-$ (base)

$$\text{pH}(\text{HCO}_3^-) = \left(\frac{\text{p}K_{a_1} + \text{p}K_{a_2}}{2} \right)$$

- (b) Similarly for H_2PO_4^- and HPO_4^{2-} amphotropic anions.

$$\text{pH}_{(\text{H}_2\text{PO}_4^-)} = \left(\frac{\text{p}K_{a_1} + \text{p}K_{a_2}}{2} \right) \quad \text{and} \quad \text{pH}_{(\text{HPO}_4^{2-})} = \left(\frac{\text{p}K_{a_2} + \text{p}K_{a_3}}{2} \right)$$



$\therefore \text{H}^+$ and OH^- also react

\therefore We can safely assume that both reactions have nearly same degree of dissociation

$$\therefore [\text{H}_2\text{CO}_3] \approx [\text{CO}_3^{2-}] \quad \dots(1)$$

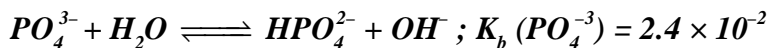
$$\frac{K_w}{K_{a_1}} = \frac{[\text{H}_2\text{CO}_3][\text{OH}^-]}{[\text{HCO}_3^-]} \Rightarrow \frac{1}{K_{a_1}} = \frac{[\text{H}_2\text{CO}_3]}{[\text{H}^+][\text{HCO}_3^-]} \quad \dots(2)$$

$$\frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]} = K_{a_2} \quad \dots(3)$$

Divide (2) by (3)

$$[\text{H}^+] = \sqrt{K_{a_1}K_{a_2}} \Rightarrow \text{pH} = \frac{\text{p}K_{a_1} + \text{p}K_{a_2}}{2}$$

Ex.29 Calculate the pH of 0.5 M Na_3PO_4 in aqueous solution ?



Sol. HPO_4^{2-} and PO_4^{3-} are conjugate acid and base so $K_a \times K_b = 10^{-14}$

$$K_a(\text{HPO}_4^{2-}) = \frac{10^{-14}}{2.4 \times 10^{-2}} = 4.17 \times 10^{-13}$$

$$\text{p}K_a = -\log K_a = 12.38$$

$$\text{or } \text{pH} = 7 + \frac{1}{2} \text{p}K_a + \frac{1}{2} \log C$$

$$\text{pH} = 13.04$$

6 BUFFER SOLUTIONS

A solution that resists change in pH value upon addition of small amount of strong acid or base or when solution is diluted is called buffer solution.

The capacity of a solution to resist alteration in its pH value is known as buffer capacity and the mechanism of buffer solution is called buffer action.

6.1 Types of buffer solutions

(A) Simple buffer solution

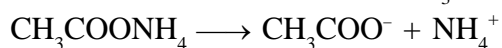
(B) Mixed buffer solution

6.2 SIMPLE BUFFER SOLUTION :

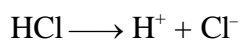
A salt of weak acid and weak base in water e.g. $\text{CH}_3\text{COONH}_4$, HCOONH_4 , AgCN , NH_4CN .

Buffer action of simple buffer solution

Consider a simple buffer solution of $\text{CH}_3\text{COONH}_4$, since it is a salt will dissociated completely.



If a strong acid such as HCl is added then

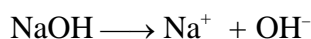


The H^+ ions from the added acid (HCl) combine with CH_3COO^- ions to form CH_3COOH , which is a weak acid so will not further ionized.

Thus there is no rise in H^+ ion concentration and the pH remains constant.



• If a strong base is added as NaOH



Thus change in OH^- ion concentration is resisted by NH_4^+ ions by forming NH_4OH which is a weak base. So it will not further ionized and pH remains constant.

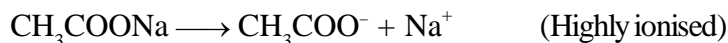
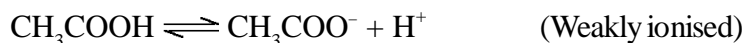
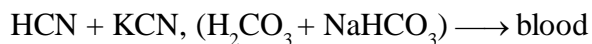
pH of a simple buffer solution :-

$$\text{pH} = 7 + \frac{1}{2} \text{p}K_a - \frac{1}{2} \text{p}K_b$$

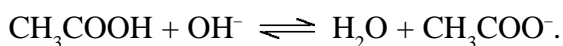
6.3 MIXED BUFFER SOLUTIONS :

6.3.1 Acidic buffer solution :

An acidic buffer solution consists of solution of a weak acid and its salt with strong base. The best known example is a mixture of solution of acetic acid and its salt with strong base (CH_3COONa). Other example :



When a few drops of an acid (HCl) are added to it, the H^+ ions from the added acid (HCl) combine with the CH_3COO^- ions to form CH_3COOH . Thus there is no rise in H^+ ion concentration and the pH of solution remains constant. On the other hand, when a few drops of base (NaOH) are added, the OH^- of the added base reacts with acetic acid to form unionised water and acetate ions.



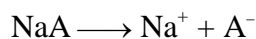
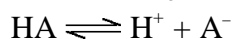
Thus there is no increase in OH^- ion concentration and hence the pH of the solution remains constant.

pH of a acidic buffer solution (Henderson equation) :

Consider a buffer mixture (acidic buffer)



where $\text{A} = \text{CH}_3\text{COO}$, $\text{A}^- = \text{CH}_3\text{COO}^-$



Applying law of mass action to dissociation equilibrium of HA

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} ; \text{ so } [\text{H}^+] = \frac{K_a[\text{HA}]}{[\text{A}^-]}$$

taking log, $\log [\text{H}^+] = \log K_a + \log \frac{[\text{HA}]}{[\text{A}^-]}$

$$-\log [\text{H}^+] = -\log K_a - \log \frac{[\text{HA}]}{[\text{A}^-]}$$

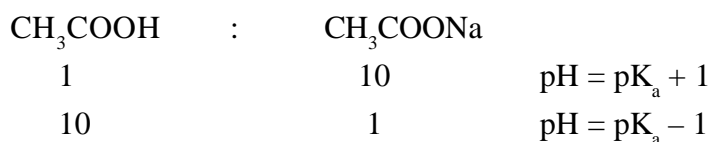
$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$[\text{A}^-]$ = Initial concentration of salt as it is mainly comes from salt.

$[\text{HA}]$ = Initial concentration of the acid.

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \quad (\text{it is known as Henderson-Hasselbalch equation.})$$

Note : A solution can act as buffer only if ratio of concentration of salt to acid is between 0.1 to 10.



Thus pH range of an acidic buffer solution is $(pK_a + 1)$ to $(pK_a - 1)$

$$\text{pH range} = pK_a \pm 1$$

Maximum buffer action will be only when ratio of concentration of acid and salt is 1. So for maximum buffer action,

$$\text{pH} = pK_a$$

Ex.30 How much volume of 0.2 M solution of acetic acid should be added to 100 mL of 0.2 M solution of sodium acetate to prepare a buffer solution of pH = 6.00 ? (pK_a for acetic acid is 4.74)

Sol. $\text{pH} = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$

$$\log \frac{[\text{Salt}]}{[\text{Acid}]} = \text{pH} - pK_a = 6.00 - 4.74 = 1.26 \quad \therefore \quad \frac{[\text{Salt}]}{[\text{Acid}]} = 18.2$$

$$\text{Moles of } \text{CH}_3\text{COONa} \text{ in solution} = \frac{100 \times 0.2}{1000} = 0.02$$

Let, volume of 0.2 acetic acid added = V mL

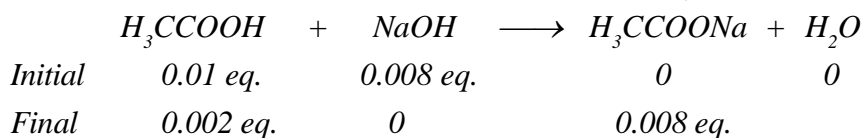
$$\therefore \quad \text{Moles of acetic acid} = \frac{V \times 0.2}{1000}$$

$$\therefore \quad \frac{0.02}{V \times \frac{0.2}{1000}} = 18.2$$

$$\therefore \quad V = 5.49 \text{ mL}$$

Ex.31 Calculate the pH after the addition of 80 mL and 100 mL respectively of 0.1 N NaOH to 100 mL, 0.1 N CH_3COOH . (Given pK_a for $\text{CH}_3\text{COOH} = 4.74$)

Sol. If 80 mL of 0.1 N NaOH is added to 100 mL of 0.1 N CH_3COOH , acidic buffer will form as



$$\text{pH} = pK_a + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 4.74 + \log \frac{0.008}{0.002} = 5.342$$

If 100 mL of 0.1 N NaOH is added to 100 mL of 0.1 N CH_3COOH , complete neutralization takes place and the concentration of $\text{H}_3\text{CCOONa} = \frac{0.1}{2} \text{ M} = 0.05 \text{ M}$

$$\text{Now, } \text{pH} = 7 + \frac{1}{2} pK_a + \frac{1}{2} \log C = 8.72$$

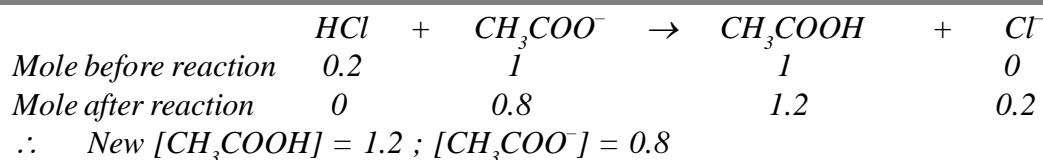
Ex.32 Calculate the pH of a solution when 0.20 moles of HCl is added to one litre solution containing -
(a) 1 M each of acetic acid and acetate ion ?
(b) 0.1 M each of acetic acid and acetate ion ?

Given K_a for acetic acid is 1.8×10^{-5} .

Sol. (a) Initially $[\text{Acetic acid}] = 1 \text{ M}$

$$[\text{Acetate}] = 1 \text{ M}$$

Now 0.2 moles of HCl are added to it.



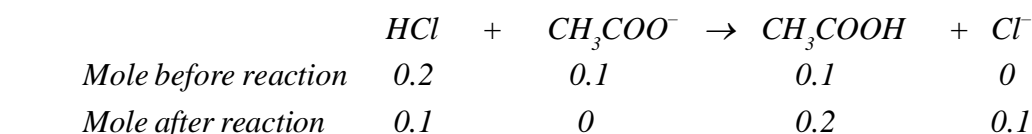
$$\therefore \text{ pH} = \text{p}K_a + \log \frac{[\text{conjugate}]}{[\text{acid}]}$$

$$\therefore \text{ pH} = -\log 1.8 \times 10^{-5} + \log \frac{0.8}{1.2} = 4.5686$$

(b) In II case initially [Acetic acid] = 0.1 M

[Acetate] = 0.1 M

Now 0.2 mole of HCl are added to it



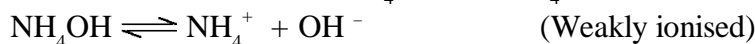
$$\therefore [\text{H}^+] \text{ from free HCl} = 0.1 \text{ M}$$

$$\therefore \text{ pH} = 1$$

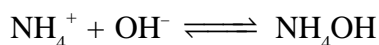
Note: CH_3COOH no doubt gives H^+ but being weak acid as well as in presence of HCl does not dissociate appreciably and thus, H^+ from CH_3COOH may be neglected.

6.3.2 Basic buffer solution :

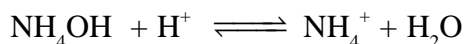
A basic buffer solution consists of a mixture of a weak base and its salt with strong acid. The best known example is a mixture of NH_4OH and NH_4Cl .



When a few drops of a base (NaOH) are added, the OH^- ions from NaOH combine with NH_4^+ ions to form feebly ionised NH_4OH thus there is no rise in the concentration of OH^- ions and hence the pH value remains constant.

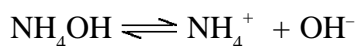


If a few drops of an acid (HCl) are added the H^+ from acid combine with NH_4OH to form H_2O and NH_4^+ ions.



Thus the addition of acid does not increase the H^+ ion concentration and hence pH remains unchanged.

• pH of basic buffer solution :



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]}$$

$$[\text{OH}^-] = \frac{K_b [\text{NH}_4\text{OH}]}{[\text{NH}_4^+]} = \frac{K_b [\text{Base}]}{[\text{Salt}]}$$

(NH_4^+ mainly comes from salt)

taking $-\log$ on both side

$$-\log \text{OH}^- = -\log \frac{K_b [\text{Base}]}{[\text{Salt}]} \Rightarrow \text{pOH} = -\log K_b - \log \frac{[\text{Base}]}{[\text{Salt}]}$$

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]} \Rightarrow \text{pH} = 14 - \text{pOH}$$

❖ **pOH range :**

A solution can act as buffer solution only if ratio of concentration of salt to base is from 0.1 to 10.

NH_4OH	:	NH_4Cl	
1		10	$\text{pOH} = \text{p}K_b + 1$
10		1	$\text{pOH} = \text{p}K_b - 1$

So pOH range is $\text{p}K_b \pm 1$

❖ **Condition for maximum buffer action :**

$[\text{NH}_4\text{OH}]$:	$[\text{NH}_4\text{Cl}]$
1		1

$$\text{pOH} = \text{p}K_b + \log \frac{1}{1}$$

$$\text{pOH} = \text{p}K_b \quad \text{and} \quad \text{pH} = 14 - \text{p}K_b$$

Maximum buffer action because pH remains constant.

Ex.33 An organic base B has K_b value equal to 1×10^{-8} . In what amounts should 0.01 M HCl and 0.01 M solution of B be mixed to prepare 1 L of a buffer solution having $\text{pH} = 7.0$?

Sol. $B + \text{H}_2\text{O} \rightleftharpoons \text{BH}^+ + \text{OH}^-$

$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[B]} = 1 \times 10^{-8}$$

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{BH}^+]}{[B]}$$

$$\Rightarrow 7 = -\log (10^{-8}) + \log \frac{[\text{BH}^+]}{[B]} \Rightarrow 7 = 8 + \log \frac{[\text{BH}^+]}{[B]}$$

$$\log \frac{[\text{BH}^+]}{[B]} = -1$$

$$\therefore \frac{[\text{BH}^+]}{[B]} = 10^{-1} = 0.1$$

Let, volume of HCl taken = xL

∴ Volume of base taken = (1 - x) L

After the reaction, millimole of BH⁺ formed = 0.01 × (x)

Millimoles of base left = 0.01 (1 - 2x)

$$\therefore \frac{[\text{BH}^+]}{[\text{B}]} = \frac{x}{[1 - 2x]} = 0.1$$

∴ x = 0.083 L = Volume of HCl

∴ Volume of base = 0.917 L

Ex.34 Which of the following buffers containing NH₄OH and NH₄Cl show the lowest pH value?

	conc. of NH ₄ OH (mol L ⁻¹)	conc. of NH ₄ Cl (mol L ⁻¹)
(A)	0.50	0.50
(B)	0.10	0.50
(C)	0.50	1.50
(D)	0.50	0.10

Sol. (B) $\text{pOH} = \text{p}K_b + \log \frac{[\text{salt}]}{[\text{base}]}$ for NH₄Cl = 0.5 and NH₄OH = 0.1

pOH will be maximum and so pH will be minimum.

Ex.35 A solution of weak base BOH was titrated with 0.1 N HCl. The pH of the solution was found to be 10.04 and 9.14 after the addition of 5 mL and 20 mL of the acid respectively. Find the dissociation constant of the base.

Sol. Case I :

	BOH	+	HCl	→	BCl	+	H ₂ O
Millimole before reac.	a		0.1 × 5 = 0.5		0		0
Millimole after reac.	(a - 0.5)		0		0.5		0.5

$$\therefore \text{pOH} = -\log K_b + \log \frac{[\text{BCl}]}{[\text{BOH}]} \dots\dots\dots(\text{i})$$

$$\therefore \text{pH} = 10.04 \quad \text{so} \quad \text{pOH} = 3.96$$

$$\therefore 3.96 = -\log K_b + \log \frac{0.5}{(a - 0.5)} \dots\dots\dots(\text{ii})$$

Case II :

	BOH	+	HCl	→	BCl	+	H ₂ O
Millimole before reac.	a		0.1 × 20 = 2		0		0
Millimole after reac.	(a - 2)		0		2		2

$$\therefore \text{pOH} = -\log K_b + \log \frac{[\text{BCl}]}{[\text{BOH}]} \dots\dots\dots(\text{iii})$$

$$\therefore \text{pH} = 9.14 \quad \therefore \text{pOH} = 4.86$$

$$\therefore 4.86 = -\log K_b + \log \frac{2}{(a-2)} \quad \dots\dots\dots(\text{iv})$$

$$\text{Solving Eqs. (ii) and (iv), } K_b = 1.81 \times 10^{-5}$$

7. INDICATORS

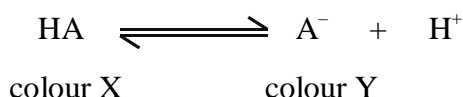
The stage of titration when complete reaction occur between the solution is called **equivalent point**.

The stage of titration when sudden change in colour of solution is observed is called **end point**. A

perfect indicator response sudden colour change exactly on completion of reaction. An **indicator** is a substance which response sudden change in colour of solution at the end point or neutral point of the

acid-base titration. **At end point** $N_1 V_1 = N_2 V_2$

- (i) The indicators in acid-base titration changes colour on changing the pH of solution.
- (ii) All the acid-base indicators are either weak organic acid or base and having different colour for unionized and ionised form.
- (iii) A mixture of two colour is recognized in a single colour if the conc. of one is 10 times or more than that of others. (This 10 time is flexible)



$$\text{Diss. const. or (Ionisation const)} = K_a = K_{in} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

$$\text{pH} = \text{p}K_{in} + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$(a) \quad \text{The solution will appear only of colour Y, if } \frac{[\text{A}^-]}{[\text{HA}]} \geq 10 \Rightarrow \text{pH} \geq (\text{p}K + 1)$$

$$(b) \quad \text{The solution will appear only of colour X, if } \frac{[\text{A}^-]}{[\text{HA}]} \leq \frac{1}{10} \Rightarrow \text{pH} \leq (\text{p}K - 1)$$

pH of solution below and above which solution appears in a single colour is called pH range of indicator.

Indicator	pH range	Colour change	pK _a
Methyl orange	3.2 – 4.5	Pink to yellow	3.7
Methyl red	4.4 – 6.5	Red to yellow	5.1
Litmus	5.5 – 7.5	Red to blue	7.0
Phenol red	6.8 – 8.4	Yellow to red	7.8
Phenolphthalein	8.3 – 10.5	Colourless to pink	9.6

Ex.36 The disso. const. of a basic indicator is 2×10^{-7} . Calculate its pH range.

Sol. $5.7 - 7.7 = \text{pOH} \quad \therefore \quad \text{pH} = 6.3 - 8.3$

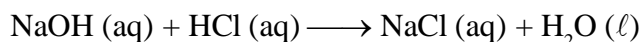
Ex.37 The pH range of an acidic indicator HIn is $4.0 - 5.2$. Calculate dissociation constant. Also

calculate $\frac{\text{In}^-}{\text{HIn}}$ for the appearance of solution in single colour.

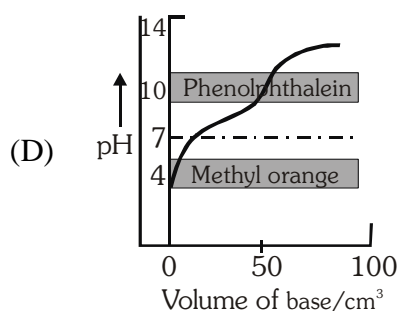
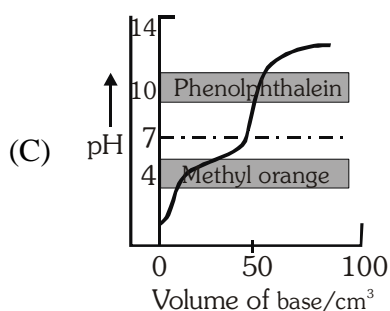
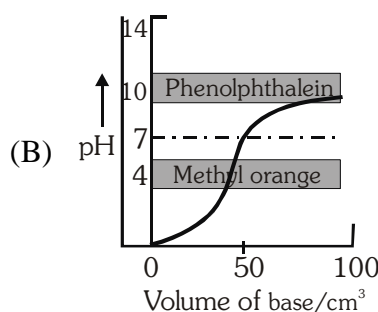
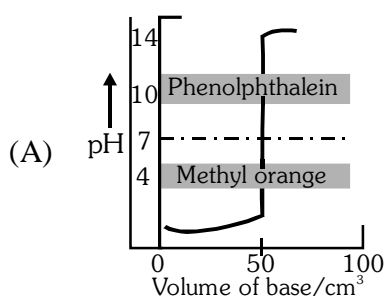
Sol. Diss. constant = 2.5×10^{-5} , 4

9.1 TITRATION OF STRONG ACID AGAINST STRONG ALKALI :

The graph (A) shows how pH changes during the titration of 50 cm^3 of 0.1 M HCl with 0.1 M NaOH .



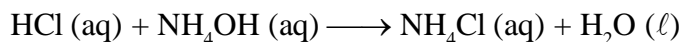
The pH of 0.1 M solution of HCl in the beginning would be 1. As alkali is added, the pH changes slowly in the beginning. However, at the equivalence point pH changes rapidly from about 3.5 to 10. It can be shown by simple calculations that pH of the solution is 3.7 when 49.8 cm^3 of 0.1 M NaOH solution have been added. The pH suddenly changes to 10 after addition of 50.1 cm^3 of the NaOH solution. Thus, any indicator having pH range between 3.5 to 10 will identify the equivalence point. This means that any one of phenolphthalein, methyl orange or bromothymol blue could be used as an indicator.



Titration curves : (A) strong base with strong acid ; (B) weak base with strong acid ; (C) strong base with weak acid ; (D) weak base with weak acid.

7.2 TITRATION OF STRONG ACID AGAINST WEAK ALKALI :

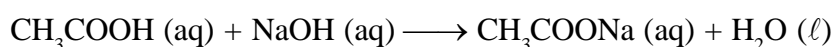
The graph (B) shows how pH changes during titration of 50 cm³ of 0.1 M HCl with 0.1 M NH₃.



In this case, the pH changes rapidly from 3.5 to 7.0 at the equivalence point. Methyl orange, methyl red and bromocresol green are suitable indicators for this type of titration. Phenolphthalein is unsuitable because its pH range lies outside the vertical portion of the curve.

7.3 TITRATION OF WEAK ACID AGAINST STRONG BASE :

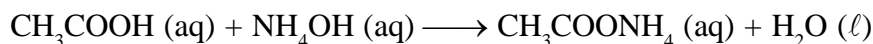
The graph (C) shows how pH changes during titration of 50 cm³ of 0.1 M CH₃COOH with 0.1 M NaOH.



The vertical portion of this titration curve lies between pH range 7 to 10.6. Phenolphthalein is suitable indicator for this titration. Methyl orange is not suitable for this titration because its pH range lies on the flat portion of the curve.

7.4 TITRATION OF WEAK ACID AGAINST WEAK BASE :

The graph (D) represents the titration curve obtained for titration of 50 cm³ of 0.1 M CH₃COOH with 0.1 M NH₃.



For this type of titration there is no sharp increase in pH at the equivalence point. No indicator is suitable for this type of titration.

Ex.38 Bromophenol blue is an indicator with a value of $K_a = 6.84 \times 10^{-6}$. At what pH it will work as an indicator? Also report the % of this indicator in its basic form at a pH of 5.84.

Sol. $\text{HBPh} \rightleftharpoons \text{H}^+ + \text{BPh}^-$

$$K_a = \frac{[\text{H}^+][\text{BPh}^-]}{[\text{HBPh}]}, \text{ when } \text{BPh}^- = \text{HBPh}, \text{ indicator will work. Thus}$$

$$[\text{H}^+] = 6.84 \times 10^{-6}$$

$$\therefore \text{pH} = 5.165$$

Also if pH = 5.84

$$\text{or } [\text{H}^+] = 1.44 \times 10^{-6}, \text{ then}$$

$$K_a = \frac{[\text{H}^+][\text{BPh}^-]}{[\text{HBPh}]} \quad \text{or} \quad 6.84 \times 10^{-6} = \frac{1.44 \times 10^{-6} \cdot C\alpha}{C(1-\alpha)} \quad \text{or} \quad \alpha = 0.83 \text{ or } 83 \%$$

7.5 Titration of Poly protic acid v/s S.B. :

50 mL of 0.1 M H_3PO_4 agent 0.1 M NaOH. Calculate pH when vol. of NaOH added is

- (a) 0 mL (b) 25 mL (c) 50 mL (d) 75 mL (e) 100 mL
 (f) 125 mL (g) 150 mL (h) 200 mL (i) 90 mL

$$pK_{a1} = 3 \quad pK_{a2} = 7, pK_{a3} = 11$$

(a) $\text{pH} = 1/2 (pK_{a1} - \log C) = 1/2 (3 + 1) = 2$



t = 0 5 Mmol 2.5 Mmol 0 –

2.5 M mol 0 2.5 M mol

$$\text{pH} = pK_{a1} + \log 1/1 = pK_{a1} = 3$$

(c) Solution of H_2PO_4^- amphoteric species

$$\text{pH} = \frac{pK_{a1} + pK_{a2}}{2} = \frac{3 + 7}{2} = 5$$



t = 0 5 M mol 2.5 M mol 0 –

2.5 M mol 2.5 M mol –

$$\text{pH} = \log 1/1 + pK_{a2} = 7$$

(e) HPO_4^{2-} solution (amphoteric species)

$$\text{pH} = \frac{pK_{a2} + pK_{a3}}{2} = 9$$



5 2.5 0 –

2.5 0 2.5 –

$$\text{pH} = pK_{a3} + \log 1/1 = 0$$

(g) 3rd eq. pt Na_3PO_4 solution

$$[\text{Na}_3\text{PO}_4] = 5/200 = 1/40$$

$$\text{pH} = 1/2 \{pK_w + pK_{a3} + \log C\} = 1/2 (14 + 11 - 2 + 0.4) = 11.7$$

(h) 200 mL

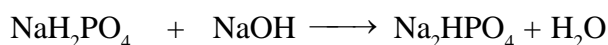
hydrolysis of Na_3PO_4 can be neglected in presence of NaOH

$$[\text{NaOH}] = 5/250 = 1/50$$

$$\text{pOH} = 1.7$$

$$\text{pH} = 12.3$$

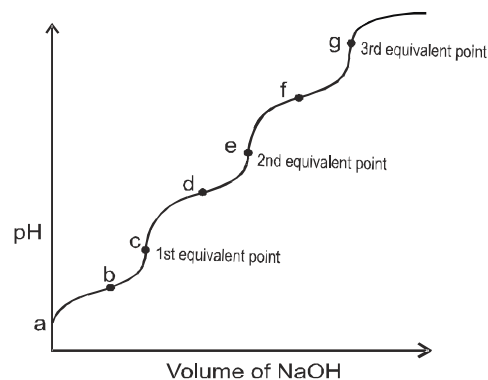
(i) 90 mL



5 4 0

1 0 4

$$\text{pH} = pK_{a2} + \log 4 = 7.6$$



10. SOLUBILITY (s) & SOLUBILITY PRODUCT (K_{sp})

10.1 SOLUBILITY :

At constant temperature, the maximum number of moles of solute which can be dissolved in a solvent to obtain 1 litre of saturated solution is called solubility.

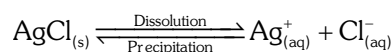
Solubility depends on the following –

- Temperature
- Presence of common ion
- Nature of solvent

10.2 SOLUBILITY PRODUCT(K_{sp}) :

When a sparingly soluble salt such as AgCl is put into water, a very small amount of AgCl dissolves in water and most of the salt remains undissolved in its saturated solution.

- A solution which remains in contact with undissolved solute is said to be saturated.
- The salt AgCl is an electrolyte, its dissociation occurs in solution. Hence, the quantity of AgCl that dissolves in water dissociates into Ag^+ and Cl^- ions. Thus, in the saturated solution of AgCl an equilibrium exists between undissolved solid AgCl and its ions, Ag^+ and Cl^- ions.



according to law of mass action

$$K = \frac{[Ag^+].[Cl^-]}{[AgCl]}$$

Since, the concentration of undissolved solid AgCl is constant. Thus, the product $K.[AgCl]$ gives another constant which is designated as K_{sp}

So, $K.[AgCl] = [Ag^+].[Cl^-]$

$\therefore K_{sp} = [Ag^+] \cdot [Cl^-]$

- K_{sp} for $CaCl_2$** $CaCl_2(s) \rightleftharpoons Ca^{+2}(aq) + 2Cl^-(aq)$

Solubility product in terms of concentration of ions

$$K_{sp} = [Ca^{+2}] [Cl^-]^2$$

- K_{sp} for $AlCl_3$** $AlCl_3(s) \rightleftharpoons Al^{+3}(aq) + 3Cl^-(aq)$

Solubility product in terms of concentration of ions $K_{sp} = [Al^{+3}] [Cl^-]^3$

- General form** $A_xB_y(s) \rightleftharpoons xA^{+y}(aq) + yB^{-x}(aq)$

$$K_{sp} = [A^{+y}]^x [B^{-x}]^y$$

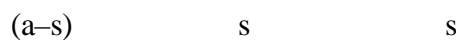
Thus, solubility product is defined as the product of concentrations of the ions raised to a power equal to the number of ions given by the dissociation of electrolyte at a given temperature when the solution is saturated.

10.3 APPLICATION OF SOLUBILITY PRODUCT (K_{sp}) :

10.3.1 To find out the solubility (S) :

- K_{sp} of AB (Mono-mono, di-di, tri-tri valency) type salt –**

Ex. NaCl, $BaSO_4$, CH_3COONa , $CaCO_3$, NaCN, KCN, NH_4CN , NH_4Cl etc.

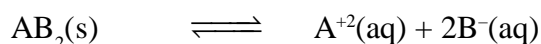


$$K_{sp} = [A^+] [B^-]$$

$$K_{sp} = s^2 \quad \text{or} \quad s = \sqrt{K_{sp}}$$

(ii) K_{sp} of AB_2 or A_2B (Mono-di or di-mono valency) type salt –

Ex. $CaCl_2$, $CaBr_2$, K_2S , $(NH_4)_2SO_4$, K_2SO_4 , K_2CO_3 etc.



$$K_{sp} = [A^{+2}] [B^-]^2$$

$$K_{sp} = s \times (2s)^2 = s \times 4s^2 = 4s^3$$

$$s = \left(\frac{K_{sp}}{4} \right)^{1/3}$$

(iii) General form :



$$K_{sp} = [A^{+y}]^x \cdot [B^{-x}]^y$$

$$K_{sp} = (xs)^x \cdot (ys)^y$$

$$K_{sp} = x^x \cdot y^y \cdot s^{(x+y)}$$

10.4 COMMON ION EFFECT ON SOLUBILITY :

Solubility of substances always decreases in the presence of common ion. According to Le-Chatelier's principle, on increasing common ion concentration equilibrium shifts in backward direction until the equilibrium is reestablished so, the solubility of substances decreases.

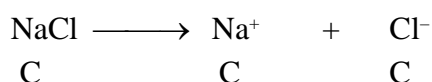
Ex. Find out the solubility of $AgCl$ in water and in the presence of CM – $NaCl$ solution?



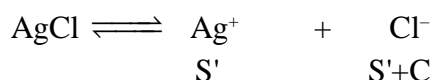
$$K_{sp} = [Ag^+] [Cl^-]$$

$$K_{sp} = S^2$$

In $NaCl$ solution



Let solubility of AgCl in the presence of NaCl solution is S' mol L^{-1}



$$K_{sp} = [\text{Ag}^+] [\text{Cl}^-]$$

$$K_{sp} = S' (S' + C) = S'^2 + S'C \quad (\text{Neglecting the higher power terms of } S')$$

$$K_{sp} = S' C$$

$$\boxed{S' = \frac{K_{sp}}{C}}$$

10.5 SIMULTANEOUS SOLUBILITY :

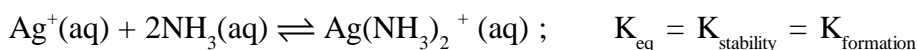
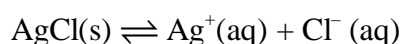
When two sparingly soluble salts are added in water simultaneously, there will be two simultaneous equilibria in the solution.

10.6 SOLUBILITY IN APPROPRIATE BUFFER SOLUTIONS :

Appropriate buffer means that the components of buffer should not interfere with the salt or only H^+ or OH^- ions should be interacting with the ions of the salt.

10.7 EFFECT ON SOLUBILITY BECAUSE OF COMPLEX FORMATION :

Solubility of AgCl in aqueous NH_3 is roughly 10,000 times as its solubility in water, due to complex formation.



$$\text{and } \frac{1}{K_{stability}} = K_{dissociation} = K_{instability}$$

10.8 CONDITION OF PRECIPITATION / IONIC PRODUCT (IP OR Q_{sp}) :

- Ionic product (IP) of an electrolyte is defined in the same way as K_{sp} . The only difference is that ionic product expression contains the initial concentration of ions or the concentration at any time whereas the expression of K_{sp} contains only equilibrium concentration. Thus, for AgCl.

$$IP = [\text{Ag}^+]_i [\text{Cl}^-]_i \quad \text{and} \quad K_{sp} = [\text{Ag}^+]_{eq} [\text{Cl}^-]_{eq}$$

- Ionic product changes with concentration but K_{sp} does not.
- To decide whether an ionic compound will precipitate, its K_{sp} is compared with the value of ionic product.

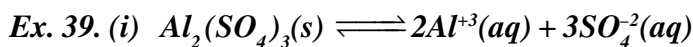
The following three cases arise :

- $IP < K_{sp}$: The solution is unsaturated and precipitation will not occur.
- $IP = K_{sp}$: The solution is saturated and solubility equilibrium exists.
- $IP > K_{sp}$: The solution is supersaturated and hence precipitation of the compound will occur.

Thus, a salt is precipitated when its ionic product exceeds the solubility product of the salt.

10.9 SELECTIVE PRECIPITATION :

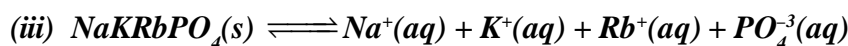
When the K_{sp} values differ then one of the salt can be selectively precipitated.



$$K_{sp} = 2^2 \times 3^3 \times (S)^{2+3} = 4 \times 27 \times S^5 = 108 S^5$$



$$K_{sp} = 2^2 \times 1^1 \times 1^1 (S)^{2+1+1} = 4S^4$$



$$K_{sp} = 1^1 \times 1^1 \times 1^1 \times 1^1 \times (S)^{1+1+1+1} = S^4$$

Ex. 40. If solubility product of the base $M(OH)_3$ is 2.7×10^{-11} , the concentration of OH^- will be

(1) 3×10^{-3}

(2) 3×10^{-4}

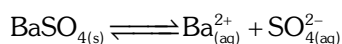
(3) 10^{-3}

(4) 10^{-11}

Answer : (3)

Ex. 41. The solubility of $BaSO_4$ in water is $1.07 \times 10^{-5} \text{ mol dm}^{-3}$. Estimate its solubility product.

Sol. Solubility equilibrium for $BaSO_4$ is

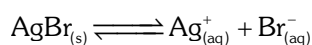


Now, $S = 1.07 \times 10^{-5} \text{ M}$

Hence, $K_{sp} = (1.07 \times 10^{-5})^2 = 1.145 \times 10^{-10}$

Ex. 42. The solubility product of $AgBr$ is 5.2×10^{-13} . Calculate its solubility in mol dm^{-3} and g dm^{-3} . (Molar mass of $AgBr$ = 187.8 g mol^{-1})

Sol. The solubility equilibrium of $AgBr$ is



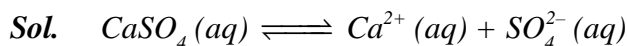
The molar solubility S of $AgBr$ is given by

$$S = \sqrt{K_{sp}} = \sqrt{5.2 \times 10^{-13}} = 7.2 \times 10^{-7} \text{ mol dm}^{-3}$$

The solubility in g dm^{-3} = molar solubility (mol dm^{-3}) \times molar mass (g mol^{-1})

$$= 7.2 \times 10^{-7} \times 187.8 = 1.35 \times 10^{-4} \text{ g dm}^{-3}$$

Ex. 43. What is the maximum volume of water required to dissolve 1 g of calcium sulphate at 25°C. For calcium sulphate, $K_{sp} = 9.0 \times 10^{-6}$.



If S is the solubility of CaSO_4 in moles L^{-1}

$$K_{sp} = [\text{Ca}^{2+}] \times [\text{SO}_4^{2-}] = S^2$$

$$\therefore S = \sqrt{K_{sp}} = \sqrt{9.0 \times 10^{-6}}$$

$$= 3 \times 10^{-3} \text{ mol L}^{-1}$$

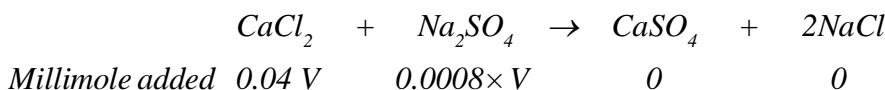
$$= 3 \times 10^{-3} \times 136 \text{ g L}^{-1} = 0.408 \text{ g L}^{-1}$$

For dissolving 0.408 g of CaSO_4 water required = 1 L

$$\therefore \text{For dissolving 1 g } \text{CaSO}_4 \text{ water required} = \frac{1}{0.408} \text{ L} = 2.45 \text{ L}$$

Ex. 44. Equal volumes of 0.04 M CaCl_2 and 0.0008 M Na_2SO_4 are mixed. Will a precipitate form? K_{sp} for $\text{CaSO}_4 = 2.4 \times 10^{-5}$

Sol.



Suppose V mL of both are mixed

$$\therefore [\text{Ca}^{2+}] = \frac{0.04 V}{2V}$$

$$[\text{SO}_4^{2-}] = \frac{0.0008 V}{2V}$$

$$\therefore [\text{Ca}^{2+}] [\text{SO}_4^{2-}] = \frac{0.04 V}{2V} \times \frac{0.0008 V}{2V} = 8 \times 10^{-6}$$

Thus, $[\text{Ca}^{2+}] [\text{SO}_4^{2-}]$ in solution $< K_{sp}$

$$8 \times 10^{-6} < 2.4 \times 10^{-5}$$

$\therefore \text{CaSO}_4$ will not precipitate.

Ex. 45. Calculate simultaneous solubility of silverthiocyanate and silver bromide in water given that k_{sp} of silver thiocyanate = 10^{-12} and k_{sp} of silver bromide = 5×10^{-13} respectively.

Sol. Let the solubility of AgSCN be x and that of AgBr is y , then



$$10^{-12} = x(x + y) \quad \dots\dots (i)$$

$$5 \times 10^{-13} = y(x + y) \quad \dots\dots (ii)$$

On solving we get, $x = 2y$

$$\text{So } y = 4.08 \times 10^{-7} \text{ and } x = 8.16 \times 10^{-7}$$

Ex. 46. What $[H^+]$ must be maintained in saturated $H_2S(0.1\text{ M})$ to precipitate CdS but not ZnS , if $[Cd^{2+}] = [Zn^{2+}] = 0.1$ initially ?

$$K_{sp} (CdS) = 8 \times 10^{-27}$$

$$K_{sp} (ZnS) = 1 \times 10^{-21}$$

$$K_a (H_2S) = 1.1 \times 10^{-21}$$

Sol. In order to prevent precipitation of ZnS

$$[Zn^{2+}][S^{2-}] < K_{sp}(ZnS) = 1 \times 10^{-21}$$

(ionic product)

$$\text{or } (0.1)[S^{2-}] < 1 \times 10^{-21}$$

$$\text{or } [S^{2-}] < 1 \times 10^{-20}$$

This is the maximum value of $[S^{2-}]$ before ZnS will precipitate. Let $[H^+]$ to maintain this $[S^{2-}]$ be x .

Thus for $H_2S \rightleftharpoons 2H^+ + S^{2-}$

$$K_a = \frac{[H^+]^2[S^{2-}]}{[H_2S]} = \frac{x^2(1 \times 10^{-20})}{0.1} = 1.1 \times 10^{-21}$$

$$\text{or } x = [H^+] = 0.1\text{ M}$$

\therefore No ZnS will precipitate at a concentration of H^+ greater than 0.1 M

Ex. 47. What must be the concentration of aq. $NH_3(\text{eq.})$ which must be added to a solution containing $4 \times 10^{-3}\text{ M Ag}^+$ and 0.001 M NaCl , to prevent the precipitation of $AgCl$.

Given that $K_{sp}(AgCl) = 1.8 \times 10^{-10}$ and the formation constant of $[Ag(NH_3)_2]^+$ is

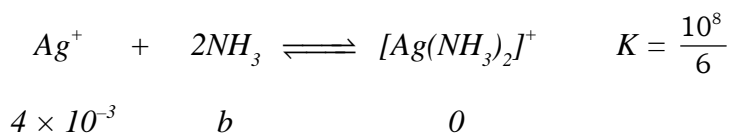
$$K_{\text{formation}} = \frac{10^8}{6}.$$

Sol. Calculate silver ion concentration which can be allowed to remain in the solution,

$$1.8 \times 10^{-10} = [Ag^+][Cl^-]$$

$$[Ag^+] = \frac{1.8 \times 10^{-10}}{0.001} = 1.8 \times 10^{-7}\text{ M},$$

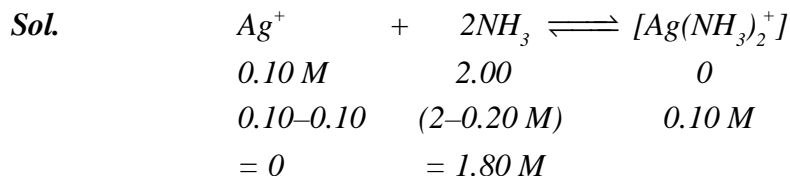
This quantity is so small that almost all the Ag^+ ion will be consumed.



$$\begin{array}{ccccccc} 1.8 \times 10^{-7} & (b - 8 \times 10^{-3}) & 4 \times 10^{-3} & K = \frac{10^8}{6} = \frac{4 \times 10^{-3}}{1.8 \times 10^{-7} \times (b - 8 \times 10^{-3})^2} \\ \Rightarrow & b = 0.0445 \end{array}$$

Ex. 48. 0.10 mol sample of AgNO_3 is dissolved in one litre of 2.00 M NH_3 . Is it possible to form $\text{AgCl}(s)$ in the solution by adding 0.010 mol of NaCl ?

$$(K_{sp}(\text{AgCl}) = 1.8 \times 10^{-10}, K_f[\text{Ag}(\text{NH}_3)_2^+] = 1.6 \times 10^7)$$



It is assumed that all Ag^+ ions have been complexed and only x amount is left

$$K_f = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2} \Rightarrow 1.6 \times 10^7 = \frac{0.10}{x(1.80)^2}$$

$$\therefore x = 1.93 \times 10^{-9} \text{ M} = [\text{Ag}^+] \text{ undissolved}$$

$$[\text{Cl}^-] = 1.0 \times 10^{-2} \text{ M}$$

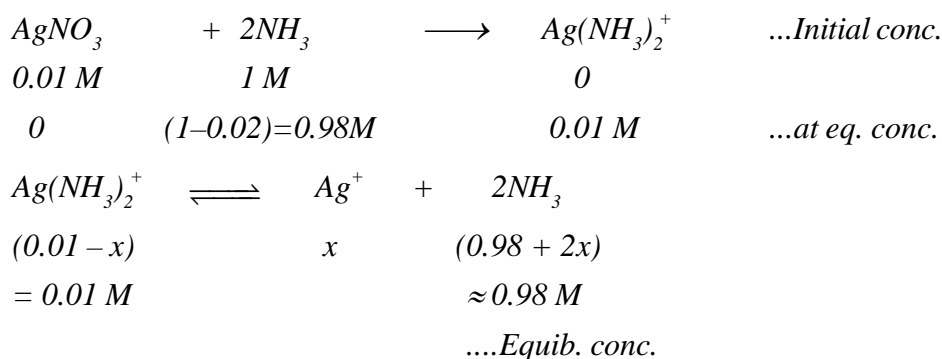
$$\therefore [\text{Ag}^+][\text{Cl}^-] = 1.93 \times 10^{-9} \times 1.0 \times 10^{-2} = 1.93 \times 10^{-11} < 1.8 \times 10^{-10} [K_{sp}(\text{AgCl})]$$

Hence, $\text{AgCl}(s)$ will not precipitate.

Ex. 49. What is the concentration of Ag^+ ions in 0.01 M AgNO_3 that is also 1.0 M NH_3 ? Will AgCl precipitate from a solution that is 0.01 M AgNO_3 , 0.01 M NaCl and 1 M NH_3 ?

$$K_d(\text{Ag}[\text{NH}_3)_2^+) = 5.88 \times 10^{-8}; K_{sp}(\text{AgCl}) = 1.8 \times 10^{-10}.$$

Sol. Let us first assume that 0.01 M AgNO_3 shall combine with 0.02 NH_3 to form 0.01 M $\text{Ag}(\text{NH}_3)_2^+$ and then consider its dissociation.



Since $x \ll 1$

$$K_d = \frac{[\text{Ag}^+][\text{NH}_3]^2}{[\text{Ag}(\text{NH}_3)_2^+]} = 5.88 \times 10^{-8}$$

$$\therefore [\text{Ag}^+] = \frac{5.88 \times 10^{-8} \times 0.01}{(0.98)^2} = 6.12 \times 10^{-10} \text{ M}$$

Further, ionic product of $\text{AgCl} = [\text{Ag}^+][\text{Cl}^-] = (6.12 \times 10^{-10})(0.01) = 6.12 \times 10^{-12}$

Because the ionic product is smaller than $K_{sp} = 1.8 \times 10^{-10}$, no precipitate should form.

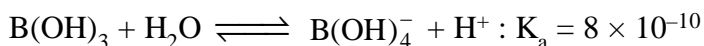
EXERCISE # S-I

IONIZATION CONSTANTS AND pH

- Q.1 Calculate the number of H^+ present in one ml of solution whose pH is 13.
- Q.2 (i) K_w for H_2O is 9×10^{-14} at $60^\circ C$. What is pH of water at $60^\circ C$. ($\log 3 = 0.47$)
 (ii) What is the nature of solution at $60^\circ C$ whose
 (a) pH = 6.7 (b) pH = 6.35
- Q.3 The value of K_w at the physiological temperature ($37^\circ C$) is 2.56×10^{-14} . What is the pH at the neutral point of water at this temperature? ($\log 2 = 0.3$)
- Q.4 Calculate pH of following solutions :
- 0.1 M HCl
 - 0.1 M CH_3COOH ($K_a = 1.8 \times 10^{-5}$) ($\log \sqrt{1.8} = 0.13$)
 - 0.1 M NH_4OH ($K_b = 1.8 \times 10^{-5}$)
 - 10^{-8} M HCl [$\sqrt{401} = (20.02)$] [$\log 1.051 = 0.03$]
 - 10^{-10} M NaOH
 - 10^{-6} M CH_3COOH ($K_a = 1.8 \times 10^{-5}$)
 - 10^{-8} M CH_3COOH ($K_a = 1.8 \times 10^{-5}$) [$\sqrt{401} = (20.02)$] [$\log 1.051 = 0.03$]
 - Decimolar solution of Baryta ($Ba(OH)_2$), diluted 100 times. ($\log 2 = 0.3$)
 - 10^{-3} mole of KOH dissolved in 100 L of water.
 - Equal volume of HCl solution (PH = 4) + 0.0019 N HCl solution
- Q.5 Calculate :
- K_a for a monobasic acid whose 0.10 M solution has pH of 4.50.
 - K_b for a monoacidic base whose 0.10 M solution has a pH of 10.50.
- Q.6 Calculate the ratio of degree of dissociation (α_2/α_1) when an acetic acid solution is diluted 100 times. Assume $\alpha \ll 1$, even on dilution. [Given $K_a = 10^{-5}$ M]
- Q.7 Calculate the ratio of degree of dissociation of acetic acid and hydrocyanic acid (HCN) in 1 M their respective solution of acids. [Given $K_{a(CH_3COOH)} = 1.8 \times 10^{-5}$; $K_{a(HCN)} = 6 \times 10^{-10}$]
- Q.8 How many moles of HCl must be removed from 1 litre of aqueous HCl solution to change its pH from 2 to 3 ?
- Q.9 pH of a dilute solution of HCl is 6.95. Calculate molarity of HCl solution.

$$\left[\begin{array}{l} 10^{-6.95} = 11.22 \times 10^{-8} \\ 10^{-7.05} = 8.90 \times 10^{-8} \end{array} \right]$$

- Q.10 The pH of aqueous solution of ammonia is 10. Find molarity of solution. $K_b(\text{NH}_4\text{OH}) = 10^{-5}$.
- Q.11 The solution of weak monoprotic acid which is 0.01 M, has pH = 3. Calculate K_a of weak acid.
- Q.12 Boric acid is a weak monobasic acid. It ionizes in water as



Calculate pH of 0.5 M boric acid.

MIXTURE OF TWO OR MORE ACIDS / BASES

- Q.13 The pH of the solution produced when an aqueous solution of strong acid pH 5 is mixed with equal volume of an aqueous solution of strong acid of pH 3 is :-
- Q.14 Calculate pH of following solutions : $[\log 0.3 = -0.522]$
- (a) 0.1 M H_2SO_4 (50 ml) + 0.4 M HCl 50 (ml)
- (b) 0.1 M HA + 0.1 M HB $[K_a(\text{HA}) = 5 \times 10^{-5} ; K_a(\text{HB}) = 4 \times 10^{-5}]$
- Q.15 Calculate pH of a solution containing 0.1M HA ($K_a = 10^{-5}$) & 0.1 M HCl.
- Q.16 Calculate $[\text{H}^+]$ and $[\text{CHCl}_2\text{COO}^-]$ in a solution that is 0.01 M in HCl and 0.01 M in CHCl_2COOH .
Take ($K_a = 3 \times 10^{-2}$) ($\sqrt{28} = 5.3$)
- Q.17 Calculate $[\text{H}^+]$, $[\text{CH}_3\text{COO}^-]$ and $[\text{C}_7\text{H}_5\text{O}_2^-]$ in a solution that is 0.02 M in acetic acid and 0.01M in benzoic acid. $K_a(\text{acetic}) = 1.8 \times 10^{-5}$, $K_a(\text{benzoic}) = 6.4 \times 10^{-5}$.

POLYPROTIC ACIDS & BASES

- Q.18 What are the concentration of H^+ , $\text{H}_2\text{C}_2\text{O}_4$, HC_2O_4^- and $\text{C}_2\text{O}_4^{2-}$ in a 0.1 M solution of oxalic acid ?

$$[K_1 = 10^{-2} \text{ M and } K_2 = 10^{-5} \text{ M}] \left[\sqrt{41} = 6.4 \right]$$

- Q.19 Calculate $[\text{H}^+]$, $[\text{H}_2\text{PO}_4^-]$, $[\text{HPO}_4^{2-}]$ and $[\text{PO}_4^{3-}]$ in a 0.01M solution of H_3PO_4 .

$$\text{Take } K_1 = 10^{-3}, K_2 = 10^{-8}, K_3 = 10^{-13}, \sqrt{41} = 6.4$$

- Q.20 Calculate pH of 0.2 M – B(OH)_2 solution.

$$(K_{b1} = 2 \times 10^{-5} ; K_{b2} = 4 \times 10^{-11}, \log 2 = 0.3)$$

HYDROLYSIS

- Q.21 What is the OH^- concentration of a 0.18 M solution of CH_3COONa . $[K_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}]$
- Q.22 Calculate the pH of a 2.0 M solution of NH_4Cl . $[K_b(\text{NH}_3) = 2 \times 10^{-5}]$
- Q.23 0.25 M solution of pyridinium chloride $\text{C}_5\text{H}_6\text{N}^+\text{Cl}^-$ was found to have a pH of 2.699. What is K_b for pyridine, $\text{C}_5\text{H}_5\text{N}$? ($\log 2 = 0.3010$)
- Q.24 Calculate the extent of hydrolysis & the pH of 0.02 M $\text{CH}_3\text{COONH}_4$.
 $[K_b(\text{NH}_3) = 1.8 \times 10^{-5}, K_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}]$
- Q.25 Calculate the percent hydrolysis in a 0.06 M solution of KCN. $[K_a(\text{HCN}) = 6 \times 10^{-10}]$

Q.26 Calculate the extent of hydrolysis of 0.005 M K_2CrO_4 . [$K_2 = 3.2 \times 10^{-7}$ for H_2CrO_4]

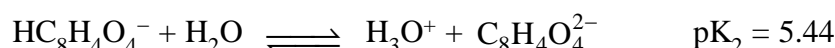
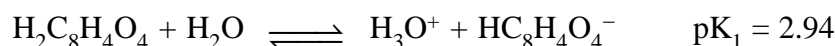
(It is essentially strong for first ionization).

Q.27 A 0.010 M solution of $PuO_2(NO_3)_2$ was found to have a pH of 4.0. What is the hydrolysis constant,

K_h , for PuO_2^{2+} , and what is K_b for PuO_2OH^+ ?

Q.28 What is the pH of 0.1M $NaHCO_3$? $K_1 = 5 \times 10^{-7}$, $K_2 = 5 \times 10^{-11}$ for carbonic acids.

Q.29 Calculate pH of 0.05M potassium hydrogen phthalate, $KHC_8H_4O_4$.



Q.30 The acid ionization (hydrolysis) constant of Zn^{2+} is 1.0×10^{-9}

(a) Calculate the pH of a 0.001 M solution of $ZnCl_2$

(b) What is the basic dissociation constant of $Zn(OH)^+$?

BUFFER SOLUTION

Q.31 Calculate the pH of solution containing 0.1M - HCN and 0.1M - NaCN. K_a of HCN = 10^{-9}

Q.32 Calculate the pH of solution containing 0.2 M - NH_4OH and 0.1 M - NH_4Cl . K_b of NH_4OH = 1.8×10^{-5} . ($\log 2 = 0.3$, $\log 1.8 = 0.26$)

Q.33 0.4 mole CH_3COONa is added in 500 ml 0.4 M - CH_3COOH solutions. What is the pH of final solution? K_a of $CH_3COOH = 1.8 \times 10^{-5}$. ($\log 2 = 0.3$, $\log 1.8 = 0.26$).

Q.34 A buffer of pH 9.26 is made by dissolving x moles of ammonium sulphate and 0.1 mole of ammonia into 100 mL solution. If pK_b of ammonia is 4.74, calculate value of x.

Q.35 Determine $[OH^-]$ of a 0.050 M solution of ammonia to which sufficient NH_4Cl has been added to make the total $[NH_4^+]$ equal to 0.100. [$K_{b(NH_3)} = 1.8 \times 10^{-5}$, $pK_b = 4.74$]

Q.36 Calculate the pH of a solution containing 0.2 M HCO_3^- and 0.1 M CO_3^{2-}

$[K_1(H_2CO_3) = 4 \times 10^{-7}$; $K_2(HCO_3^-) = 4 \times 10^{-11}]$

Q.37 Calculate the pH of a solution prepared by mixing 50.0 mL of 0.200 M $HC_2H_3O_2$ and 50.0 mL of 0.100 M NaOH. [$K_a(CH_3COOH) = 1.8 \times 10^{-5}$, $pK_a = 4.74$]

Q.38 50 mL of 0.1 M NaOH is added to 75 mL of 0.1 M NH_4Cl to make a basic buffer. If pK_a of NH_4^+ is 9.26, calculate pH.

Q.39 Calculate the pH of a solution which results from the mixing of 50.0 ml of 0.3 M HCl with 50.0 ml of 0.4 M NH_3 . [$K_b(NH_3) = 1.8 \times 10^{-5}$, $pK_b = 4.74$]

Q.40 In 100 ml buffer solution of 0.1M CH_3COOH & 0.1M CH_3COONa , how many millimoles of NaOH should be added to increase its pH by 0.3.

Given ($\log 2 = 0.3$)

ACID BASE REACTIONS & TITRATIONS

Q.41 Calculate OH^- concentration at the equivalent point when a solution of 0.2 M acetic acid is titrated with a solution of 0.2 M NaOH. K_a for the acid = 10^{-5} .

Q.42 Calculate the hydronium ion concentration and pH at the equivalence point in the reaction of 22.0 mL of 0.10M acetic acid, CH_3COOH , with 22.0 mL of 0.10 M NaOH. [$K_a = 2 \times 10^{-5}$]

Q.43 Calculate the hydronium ion concentration and the pH at the equivalence point in a titration of 50.0 mL of 0.40 M NH_3 with 0.40M HCl. [$K_b = 2 \times 10^{-5}$]

Q.44 CH_3COOH (50 ml, 0.1 M) is titrated against 0.1 M NaOH solution. Calculate the pH at the addition of 0 ml, 10 ml 20 ml, 25 ml, 40 ml, 50 ml of NaOH. K_a of CH_3COOH is 2×10^{-5} .
[$\log 2 = 0.3010$, $\log 3 = 0.4771$]

INDICATORS

Q.45 For the acid indicator thymol blue, pH is 3 when half the indicator is in unionised form. Find the % of indicator in unionised form in the solution with $[\text{H}^+] = 4 \times 10^{-3}$ M.

Q.46 Bromophenol blue is an acid indicator with a K_a value of 6×10^{-5} . What % of this indicator is in its basic form at a pH of 5 ?

Q.47 At what pH does an indicator change colour if the indicator is a weak acid with $K_{\text{ind}} = 4 \times 10^{-4}$. For which one(s) of the following neutralizations would the indicator be useful ? Explain.

(a) $\text{NaOH} + \text{CH}_3\text{COOH}$ (b) $\text{HCl} + \text{NH}_3$ (c) $\text{HCl} + \text{NaOH}$

Q.48 An acid indicator has a K_a of 3×10^{-5} . The acid form of the indicator is red & the basic form is blue. By how much must the pH change in order to change the indicator form 75% red to 75 % blue? [$\log 3 = 0.4771$]

SOLUBILITY & SOLUBILITY PRODUCT'S

Q.49 The values of K_{sp} for the slightly soluble salts MX and QX_2 are each equal to 4.0×10^{-18} . Which salt is more soluble? Explain your answer fully.

Q.50 The solubility of PbSO_4 in water is 0.0608 g/L. Calculate the solubility product constant of PbSO_4 .
Molar mass $\text{PbSO}_4 = 304$ g/mole

Q.51 How many mole CuI ($K_{\text{sp}} = 5 \times 10^{-12}$) will dissolve in 1.0 L of 0.10 M NaI solution ?

Q.52 A solution of saturated CaF_2 is found to contain 4×10^{-4} M fluoride ion. Calculate the K_{sp} of CaF_2 . Neglect hydrolysis.

Q.53 The solubility of ML_2 (formula weight = 60 g/mol) in water is 2.4×10^{-5} g/100 mL solution. Calculate the solubility product constant for ML_2 .

- Q.54 Calculate the solubility of A_2X_3 in pure water, assuming that neither kind of ion reacts with water. For A_2X_3 , $K_{sp} = 1.08 \times 10^{-23}$
- Q.55 Determine the solubility of AgCl in 0.1 M $BaCl_2$. [K_{sp} for AgCl = 1×10^{-10}]
- Q.56 Calculate solubility of $Ca_3(PO_4)_2$ ($K_{sp} = 10^{-15}$) in presence of 0.1 M $CaCl_2$ solution.

SIMULTANEOUS SOLUBILITY

- Q.57 Calculate the Simultaneous solubility of AgSCN and AgBr. K_{sp} (AgSCN) = 3.2×10^{-12} , K_{sp} (AgBr) = 8×10^{-13} .
- Q.58 Calculate F^- in a solution saturated with respect of both MgF_2 and SrF_2 . $K_{sp}(MgF_2) = 9.5 \times 10^{-9}$, $K_{sp}(SrF_2) = 4 \times 10^{-9}$.

COMPLEX FORMATION

- Q.59 Calculate the solubility of AgCl in 0.2 M - NH_3 solution.
Given : K_{sp} of AgCl = 2×10^{-10} , K_f of $Ag(NH_3)_2^+ = 8 \times 10^6$.
- Q.60 Calculate the solubility of AgCN in 0.4 M - KCN solution
(i) neglecting complex formation
(ii) considering complex formation. Given : K_{sp} of AgCN = 8×10^{-10} , K_d of $Ag(CN)_2^- = 4 \times 10^{-8}$.

SOLUBILITY, CONSIDERING HYDROLYSIS

- Q.61 Calculating the solubility of MX in water. Also calculate pH of solution.
Given : K_{sp} of MX = 4×10^{-8} ; K_a of HX = 2×10^{-6} and MOH is strong base.
- Q.62 Calculate the solubility of AgCN in a buffer solution at pH = 3.0. .
Given : K_{sp} of AgCN = 8×10^{-10} , K_a of HCN = 5×10^{-10} .

PRECIPITATION

- Q.63 A solution has a Mg^{2+} concentration of 0.0010 mol/L. Will $Mg(OH)_2$ precipitate if the OH^- concentration of the solution is [$K_{sp} = 1.2 \times 10^{-11}$]
(a) 10^{-5} mol/L (b) 10^{-3} mol/L ?
- Q.64 200 ml of 2×10^{-4} M - $AgNO_3$ solution is mixed with 400 ml of 1.2×10^{-6} M - NaCl solution. Predict whether precipitation of AgCl will occur or not. K_{sp} of AgCl = 2×10^{-10} .
- Q.65 Calculate the minimum mass of Na_2SO_4 needed to just start precipitation of $BaSO_4$ from 500 ml of 2×10^{-5} M - $BaCl_2$ solution. K_{sp} of $BaSO_4 = 8 \times 10^{-8}$.

EXERCISE # S-II

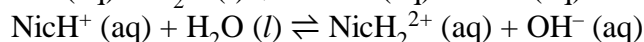
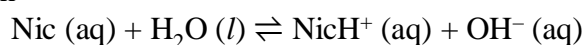
- Q.1 What are the concentrations of H^+ , HSO_4^- , SO_4^{2-} and H_2SO_4 in a 0.20 M solution of sulphuric acid?

Given : $\text{H}_2\text{SO}_4 \longrightarrow \text{H}^+ + \text{HSO}_4^-$; strong



- Q.2 Calculate the pH of a 0.1M solution of $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$; ethylenediamine (en). Determine the H_2^{2+} concentration in the solution. K_{b1} and K_{b2} values of ethylenediamine are 9×10^{-5} and 7.1×10^{-8} respectively.

- Q.3 Nicotine, $\text{C}_{10}\text{H}_{14}\text{N}_2$, has two basic nitrogen atoms and both can react with water to give a basic solution



K_{b1} is 8×10^{-7} and K_{b2} is 10^{-10} . Calculate the approximate pH of a 0.20 M solution.

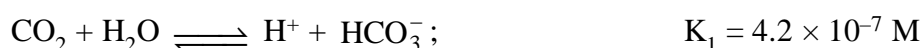
- Q.4 Determine the $[\text{S}^{2-}]$ in a saturated (0.1M) H_2S solution to which enough HCl has been added to produce a $[\text{H}^+]$ of 2×10^{-4} . $K_1 = 10^{-7}$, $K_2 = 10^{-14}$.

- Q.5 An aqueous solution contains 0.01 M RNH_2 ($K_b = 2 \times 10^{-6}$) & 10^{-4} M NaOH. The concentration of OH^- is nearly :

- Q.6 Calculate the pH of 1.0×10^{-3} M sodium phenoxide, NaOC_6H_5 . K_a for HOC_6H_5 is 0.6×10^{-10} .

- Q.7 Calculate the OH^- concentration and the H_3PO_4 concentration of a solution prepared by dissolving 0.1 mol of Na_3PO_4 in sufficient water to make 1L of solution. $K_1 = 7.1 \times 10^{-3}$, $K_2 = 6.3 \times 10^{-8}$, $K_3 = 4.5 \times 10^{-13}$.

- Q.8 Calculate the pH of 0.1 M solution of (i) NaHCO_3 , (ii) Na_2HPO_4 and (iii) NaH_2PO_4 . Given that:



($\log 4.2 = 0.62$, $\log 4.8 = 6.8$, $\log 6.2 = 0.80$, $\log 7.5 = 0.88$)

- Q.9 An ammonia-ammonium chloride buffer has a pH value of 9 with $[\text{NH}_3] = 0.25$. What will be the new pH if 500 ml 0.1 M KOH is added to 200 ml buffer solution ($K_b = 2 \times 10^{-5}$)
[$\log 2 = 0.3$]

- Q.10 A weak base (50.0mL) was titrated with 0.1 M HCl. The pH of the solution after the addition of 10.0 mL and 25.0 mL were found to be 9.84 and 9.24, respectively. Calculate K_b of the base and pH at the equivalence point. [$\log 2 = 0.3$]

- Q.11 A weak acid (50.0mL) was titrated with 0.1 M NaOH. The pH values when 10.0 mL and 25.0 mL of base have been added are found to be 4.16 and 4.76, respectively. Calculate K_a of the acid and pH at the equivalence point. [$\log 2 = 0.3$]

- Q.12 10 ml of 0.1M weak acid HA ($k_a = 10^{-5}$) is mixed with 10 ml 0.2M HCl and 10 ml 0.1M NaOH . Find the value of $[\text{A}^-]$ in the resulting solution.
- Q.13 150 ml of 0.5 M HCN ($K_a = 3.75 \times 10^{-9}$) was reacted with 1.5 M KOH for complete neutralisation. What will be molarity of HCN at equilibrium.
- Q.14 The indicator phenol red is half in the ionic form when pH is 7.2. If the ratio of the undissociated form to the ionic form is 1 : 5, find the pH of the solution. With the same pH for solution, if indicator is altered such that the ratio of undissociated form to dissociated form becomes 1 : 4, find the pH when 50 % of the new indicator is in ionic form. $[\log 2 = 0.3]$
- Q.15 How much AgBr could dissolve in 1.0 L of 0.40 M NH_3 ? Assume that $\text{Ag}(\text{NH}_3)_2^+$ is the only complex formed. $[K_f(\text{Ag}(\text{NH}_3)_2^+) = 1 \times 10^8; K_{sp}(\text{AgBr}) = 5 \times 10^{-13}]$
 $[\sqrt{50} \approx 7]$
- Q.16 Calculate solubility of PbI_2 ($K_{sp} = 1.4 \times 10^{-8}$) in water at 25° , which is 90% dissociated.
- $$\left(\frac{1.4}{(0.81)(3.6)} \right)^{1/3} = 0.78$$
- Q.17 A recent investigation of the complexation of SCN^- with Fe^{3+} led to 130, 16, and 1.0 for K_1 , K_2 , and K_3 , respectively. What is the overall formation constant of $\text{Fe}(\text{SCN})_3$ from its component ions, and what is the dissociation constant of $\text{Fe}(\text{SCN})_3$ into its simplest ions on the basis of these data ?

EXERCISE # O-I

Single correct

- Q.1 The conjugate acid of NH_2^- is
 (A) NH_3 (B) NH_2OH (C) NH_4^+ (D) N_2H_4
- Q.2 Which of the following is not a Bronsted acid:-
 (A) CH_3NH_4^+ (B) CH_3COO^- (C) H_2O (D) HSO_4^-
- Q.3 In the reaction
 $\text{HNO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{NO}_3^-$, the conjugate base of HNO_3 is :-
 (A) H_2O (B) H_3O^+ (C) NO_3^- (D) H_3O^+ and NO_3^-
- Q.4 Out of the following, amphiprotic species in aqueous medium are
 I: HPO_3^{2-} II OH^- III H_2PO_4^- IV HCO_3^-
 (A) I, III, IV (B) I and III (C) III and IV (D) All
- Q.5 When ammonia is added to water, it decreases the concentration of which of the following ion
 (A) OH^- (B) H_3O^+ (C) NH_4^+ (D) NH_4^+ & OH^-
- Q.6 Which of the following pair is Lewis acid & Lewis base & Product of these is also Lewis base
 (A) BF_3 , NH_3 (B) SiCl_4 , 2Cl^- (C) CH_3^\oplus , $^\ominus\text{OC}_2\text{H}_5$ (D) All of these
- Q.7 Ionic product of water will increase, if :-
 (A) Pressure is decreased (B) H^+ is added
 (C) OH^- is increased (D) Temperature is increased
- Q.8 At 60°C , pure water has $[\text{H}_3\text{O}^+] = 10^{-6.7} \text{ mol/lit.}$ what is the value of K_w at 60°C :-
 (A) 10^{-6} (B) 10^{-12} (C) 10^{-67} (D) $10^{-13.4}$
- Q.9 Liquid NH_3 ionises to a slight extent. At a certain temperature its self ionization constant $K_{\text{SIC}(\text{NH}_3)} = 10^{-30}$. The number of NH_4^+ ions present per 100 cm^3 of pure liquid are
 (A) 10^{-15} (B) 6.022×10^8 (C) 6.022×10^7 (D) None
- Q.10 The pH of solution is increased from 3 to 6. Its H^+ ion conc. will be :-
 (A) Reduced to half (B) Doubled
 (C) Reduced by 1000 times (D) Increased by 1000 times
- Q.11. pOH of $[1/200] \text{ mol/m}^3 \text{ H}_2\text{SO}_4 \text{ (aq.)}$ solution at 25°C is-
 (A) 2 (B) 5 (C) 9 (D) 12
- Q.12 Degree of dissociation of 0.1 N CH_3COOH is :- (Dissociation constant = 1×10^{-5})
 (A) 10^{-5} (B) 10^{-4} (C) 10^{-3} (D) 10^{-2}
- Q.13 The pH of a 0.02 M ammonia solution which is 5% ionised will be :-
 (A) 2 (B) 11 (C) 5 (D) 7
- Q.14 The pH of an aqueous solution of 1.0 M solution of a weak monoprotic acid which is 1% ionised is
 (A) 1 (B) 2 (C) 3 (D) 11
- Q.15 The concentration of $[\text{H}^+]$ and concentration of $[\text{OH}]^-$ of a 0.1 M aqueous solution of 2% ionised weak acid is [ionic product of water = 1×10^{-14}]
 (A) $0.02 \times 10^{-3} \text{ M}$ and $5 \times 10^{-11} \text{ M}$ (B) $1 \times 10^{-3} \text{ M}$ and $3 \times 10^{-11} \text{ M}$
 (C) $2 \times 10^{-3} \text{ M}$ and $5 \times 10^{-12} \text{ M}$ (D) $3 \times 10^{-2} \text{ M}$ and $4 \times 10^{-13} \text{ M}$

- Q.16 What is the quantity of NaOH present in 250 cc of the solution, so that it gives a pH = 13 :-
 (A) 10^{-13} g (B) 10^{-1} g (C) 1.0 g (D) 4.0 g
- Q.17 An aqueous solution of HCl is 10^{-9} M HCl. The pH of the solution should be:-
 (A) 9 (B) Between 6 and 7 (C) 7 (D) Unpredictable
- Q.18. The moles of H^+ from H_2O in a 1l, $\sqrt{5} \times 10^{-7}$ M HCl solution at $25^\circ C$, is
 ($\sqrt{5} = 2.23$)
 (A) 10^{-7} (B) 6.85×10^{-8} (C) 3.85×10^{-8} (D) 10^{-8}
- Q.19 Which one of the following has highest pH:-
 (A) Distilled water (B) 1 M NH_3
 (C) 1 M NaOH (D) Water saturated with chlorine
- Q.20 8 gm NaOH and 4.9 gm H_2SO_4 are present in one litre of the solution. What is its pH
 (A) 1 (B) 13 (C) 12 (D) 2
- Q.21 10 ml of $\frac{M}{200} H_2SO_4$ is mixed with 40 ml of $\frac{M}{200} H_2SO_4$. The pH of the resulting solution is
 (A) 1 (B) 2 (C) 2.3 (D) none of these
- Q.22 Which of the following solution will have pH close to 1.0?
 (A) 100 ml of M/100 HCl + 100 ml of M/10 NaOH
 (B) 55 ml of M/10 HCl + 45 ml of M/10 NaOH
 (C) 10 ml of M/10 HCl + 90 ml of M/10 NaOH
 (D) 75 ml of M/5 HCl + 25 ml of M/5 NaOH
- Q.23 A solution with pH 2.0 is more acidic than the one with pH 6.0 by a factor of:
 (A) 3 (B) 4 (C) 3000 (D) 10000
- Q.24 The first and second dissociation constants of an acid H_2A are 1.0×10^{-5} and 5.0×10^{-10} respectively. The overall dissociation constant of the acid will be :
 (A) 5.0×10^{-5} (B) 5.0×10^{15} (C) 5.0×10^{-15} (D) 0.2×10^5
- Q.25 If pK_b for fluoride ion at $25^\circ C$ is 10.4, the ionisation constant of hydrofluoric acid in water at this temperature is :
 (A) 4×10^{-11} (B) 3×10^{-3} (C) 2.5×10^{-4} (D) 2×10^{-2}
- Q.26 pH of an aqueous solution of NaCl at $85^\circ C$ should be
 (A) 7 (B) > 7 (C) < 7 (D) 0
- Q.27 1 cc of 0.1 N HCl is added to 99 cc solution of NaCl. The pH of the resulting solution will be
 (A) 7 (B) 3 (C) 4 (D) 1
- Q.28 The degree of hydrolysis of a salt of weak acid and weak base in its 0.1 M solution is found to be 50%. If the molarity of the solution is 0.2 M, the percentage hydrolysis of the salt should be
 (A) 100% (B) 50% (C) 25% (D) none of these
- Q.29 What is the percentage hydrolysis of NaCN in N/80 solution when the dissociation constant for HCN is 2×10^{-9} and $K_w = 1.0 \times 10^{-14}$
 (A) 2 (B) 5.26 (C) 8.2 (D) 9.6

- Q.30 The compound whose 0.1 M solution is basic is
 (A) Ammonium acetate (B) Ammonium chloride
 (C) Ammonium sulphate (D) Sodium acetate
- Q.31 If equilibrium constant of
 $\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+$
 is 1.8×10^{-5} , equilibrium constant for
 $\text{CH}_3\text{COOH} + \text{OH}^- \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_2\text{O}$ is
 (A) 1.8×10^{-9} (B) 1.8×10^9 (C) 5.55×10^{-9} (D) 5.55×10^{10}
- Q.32 The pK_a of a weak acid, HA, is 4.80. The pK_b of a weak base, BOH, is 4.78. The pH of an aqueous solution of the corresponding salt, BA, will be :
 (A) 8.58 (B) 4.79 (C) 7.01 (D) 9.22
- Q.33 The highest pH value is of :-
 (A) 0.1 M NaCl (B) 0.1 M NH_4Cl
 (C) 0.1 M CH_3COONa (D) 0.1 M $\text{CH}_3\text{COONH}_4$
- Q.34 pH of K_2S solution is:-
 (A) 7 (B) Less than 7 (C) More than 7 (D) 0
- Q.35 Degree of Hydrolysis of $\frac{N}{100}$ solution of KCN is (Given $K_a = 1.6 \times 10^{-9}$)
 (A) 2.5×10^{-3} (B) 2.5×10^{-2} (C) 2.5×10^{-4} (D) 2.5×10^{-5}
- Q.36 A solution of FeCl_3 in water acts as acidic due to :-
 (A) Acidic impurities (B) Ionisation (C) Hydrolysis of Fe^{3+} (D) Dissociation
- Q.37 If 40 ml of 0.2 M KOH is added to 160 ml of 0.1 M HCOOH [$K_a = 2 \times 10^{-4}$], the pOH of the resulting solution is
 (A) 3.4 (B) 3.7 (C) 7 (D) 10.3
- Q.38 1 M NaCl and 1M HCl are present in an aqueous solution. The solution is
 (A) not a buffer solution and with $\text{pH} < 7$
 (B) not a buffer solution with $\text{pH} > 7$
 (C) a buffer solution with $\text{pH} < 7$
- Q.39 The pK_a of a weak acid (HA) is 4.5. The pOH of an aqueous buffered solution of HA in which 50% of the acid is ionized is :
 (A) 4.5 (B) 2.5 (C) 9.5 (D) 7.0
- Q.40 To a 50 ml. of 0.05M formic acid, how much volume of 0.10M sodium formate must be added to get a buffer solution of $\text{pH} = 4.0$?
 (pK_a of the acid is 3.7) ($\log 2 = 0.3$)
 (A) 40 ml. (B) 4 ml. (C) 50 ml. (D) 100 ml.
- Q.41 Which can act as buffer :-
 (A) $\text{NH}_4\text{OH} + \text{NaOH}$
 (B) $\text{HCOOH} + \text{HCl}$
 (C) 40 ml. of 0.1 M NaCN + 20 ml. of 0.1 M HCl
 (D) All of them

- Q.42 If equal volume of 0.05 M ammonium hydroxide solution is dissolved in 0.001 M ammonium chloride solution. What will be the OH^- ion concentration of this solution :
 $K_b(\text{NH}_4\text{OH}) = 1.8 \times 10^{-5}$
 (A) 3.0×10^{-3} (B) 4.6×10^{-4} (C) 9.0×10^{-3} (D) 9.0×10^{-4}
- Q.43 Calculate the pH of a buffer prepared by mixing 600 cc of 0.6 M NH_3 and 400 cc of 0.5 M NH_4Cl .
 K_b for $\text{NH}_3 = 1.8 \times 10^{-5}$, ($\log 1.8 = 0.26$)
 (A) 11.3 (B) 9.0 (C) 9.52 (D) 5
- Q.44 pK_b for NH_4OH at certain temperature is 4.74. The pH of basic buffer containing equimolar concentration of NH_4OH and NH_4Cl will be:-
 (A) 7.74 (B) 4.74 (C) 2.37 (D) 9.26
- Q.45 On addition of NaOH to CH_3COOH solution, 60% of the acid is neutralised. If pK_a of CH_3COOH is 4.7 then the pH of the resulting solution is :-
 (A) More than 4.7 but less than 5.0 (B) Less than 4.7 but more than 4.0
 (C) More than 5.0 (D) Remains unchanged
- Q.46 Henderson equation $\text{pH} - \text{pK}_a = 5$ will be applicable to an acidic buffer when :-
 (A) $[\text{Acid}] = [\text{Conjugate base}]$ (B) $[\text{Acid}] \times 10^5 = [\text{Conjugate base}]$
 (C) $[\text{Acid}] = [\text{Conjugate base}] \times 10^5$ (D) $[\text{acid}] = 2 [\text{conjugate base}]$
- Q.47 What amount of sodium propanoate should be added to one litre of an aqueous solution containing 0.02 mole of propanoic acid ($K_a = 3 \times 10^{-5}$ at 25°C) to obtain a buffer solution of pH 4.7
 (A) 4.52×10^{-2} mol (B) 3.52×10^{-2} mol
 (C) 2.52×10^{-2} mol (D) 3×10^{-2} mol
- Q.48 In a buffer solution the ratio of concentration of NH_4Cl and NH_4OH is 1 : 1. When it changes in 2 : 1, what will be the value of pH of buffer ?
 (A) Increase (B) Decrease (C) No effect (D) None
- Q.49 The buffer solution play an important role in :-
 (A) Increasing the pH value (B) Decreasing the pH value
 (C) Keeping the pH constant (D) Solution will be neutral
- Q.50 The total number of different kind of acidic buffers obtained during the titration of H_3PO_4 with NaOH are :
 (A) 3 (B) 1 (C) 2 (D) 0
- Q.51 Which of the following solutions does not act as buffer :
 (A) $\text{H}_3\text{PO}_4 + \text{NaH}_2\text{PO}_4$ (B) $\text{NaHCO}_3 + \text{H}_2\text{CO}_3$
 (C) $\text{NH}_4\text{Cl} + \text{HCl}$ (D) $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$
- Q.52 Half of the formic acid solution is neutralised on addition of a KOH solution to it. If $K_a(\text{HCOOH}) = 2 \times 10^{-4}$ then pH of the solution is : - ($\log 2 = 0.3010$)
 (A) 3.6990 (B) 10.3010 (C) 3.85 (D) 4.3010
- Q.53 When 0.02 moles of NaOH are added to a litre of buffer solution, its pH changes from 5.75 to 5.80. What is its buffer capacity :-
 (A) 0.4 (B) 0.05 (C) - 0.05 (D) 2.5

- Q.54 Calculate pH when 100 ml of 0.2M NaOH is reacted with 100 ml of 0.2 M CH_3COOH ($K_a = 10^{-5}$)
 (A) 9 (B) 7 (C) 5 (D) 2
- Q.55 At 90°C , pure water has $[\text{H}^+] = 10^{-6}\text{ M}$, if 100 ml of 0.2 M HNO_3 is added to 20 ml of 1 M NaOH at 90°C then pH of the resulting solution will be
 (A) 5 (B) 6 (C) 7 (D) None of these
- Q.56 When 20 ml of $\frac{\text{M}}{20}$ NaOH are added to 10 ml of $\frac{\text{M}}{10}$ HCl, the resulting solution will:-
 (A) Turn blue litmus red
 (B) Turn phenolphthalein solution pink colour
 (C) Turn methyl orange red
 (D) Will have no effect on either red or blue litmus
- Q.57 The rapid change of pH near the stoichiometric point of an acid-base titration is the basis of indicator detection. pH of the solution is related to ratio of the concentrations of the conjugate acid (HIn) and base (In^-) forms of the indicator by the expression :-
 (A) $\log \frac{[\text{HIn}]}{[\text{In}^-]} = \text{pK}_{\text{In}} - \text{pH}$ (B) $\log \frac{[\text{HIn}]}{[\text{In}^-]} = \text{pH} - \text{pK}_{\text{In}}$
 (C) $\log \frac{[\text{In}^-]}{[\text{HIn}]} = \text{pH} + \text{pK}_{\text{In}}$ (D) $\log \frac{[\text{In}^-]}{[\text{HIn}]} = \text{pK}_{\text{In}} - \text{pH}$
- Q.58 Calculate the pH range in which an acid indicator with $K_{\text{acid}} (\text{indicator}) = 1.0 \times 10^{-5}$ changes colour when the concentration of the indicator is $1 \times 10^{-3}\text{ M}$.
 (A) 5 ± 1 (B) 11 ± 1 (C) 3 ± 1 (D) 8 ± 1
- Q.59 In what pH range will a $1 \times 10^{-4}\text{ M}$ solution of an indicator will $K_b (\text{indicator}) = 1 \times 10^{-11}$ change colour?
 (A) 7.0 ± 1 (B) 3.0 ± 1 (C) 5.5 ± 1 (D) 11.0 ± 1
- Q.60 Indicator which is used in the titration of CH_3COOH & NaOH :-
 (A) Methyl orange (B) Methyl red (C) Phenolphthalein (D) Litmus
- Q.61 Phenolphthalein is a :-
 (A) Strong acid (B) Strong base (C) Weak base (D) Weak acid
- Q.62 pH-range of Methyl red indicator is :-
 (A) 4.2–6.2 (B) 6.8–10.8 (C) 8 – 9.6 (D) 6.8 – 8.2
- Q.63 In the volumetric estimation of HCl, if we make use of phenolphthalein as an indicator, which base is unsuitable for the titration :-
 (A) NaOH (B) RbOH (C) KOH (D) NH_4OH
- Q.64 Phenolphthalein does not act as an indicator for the titration between :-
 (A) KOH and H_2SO_4 (B) NaOH and CH_3COOH
 (C) Oxalic acid and KMnO_4 (D) $\text{Ba}(\text{OH})_2$ and HCl
- Q.65 For weak acid and strong base titration, the indicator used is :-
 (A) Potassium di-chromate (B) Methyl orange
 (C) Litmus (D) Phenolphthalein

- Q.66 The solubility of A_2X_3 is $y \text{ mol dm}^{-3}$. Its solubility product is
 (A) $6y^2$ (B) $64y^4$ (C) $36y^5$ (D) $108y^5$
- Q.67 If K_{sp} for $HgSO_4$ is 6.4×10^{-5} , then solubility of this substance in mole per m^3 is
 (A) 8×10^{-3} (B) 6.4×10^{-5} (C) 8×10^{-6} (D) 8
- Q.68 If the solubility of $AgCl$ (formula mass=143) in water at $25^\circ C$ is $1.43 \times 10^{-4} \text{ gm/100 ml}$ of solution then the value of K_{sp} will be :-
 (A) 1×10^{-5} (B) 2×10^{-5} (C) 1×10^{-10} (D) 2×10^{-10}
- Q.69 One litre of saturated solution of $CaCO_3$ is evaporated to dryness, 7.0 g of residue is left. The solubility product for $CaCO_3$ is:-
 (A) 4.9×10^{-3} (B) 4.9×10^{-5} (C) 4.9×10^{-9} (D) 4.9×10^{-7}
- Q.70 A_3B_2 is a sparingly soluble salt of molar mass $M \text{ (g mol}^{-1}\text{)}$ and solubility $x \text{ g lit}^{-1}$. The ratio of the molar concentration of B^{3-} to the solubility product of the salt is
 (A) $108 \frac{x^5}{M^5}$ (B) $\frac{1}{108} \frac{M^4}{x^4}$ (C*) $\frac{1}{54} \frac{M^4}{x^4}$ (D) None
- Q.71. Solubility of Ag_2CrO_4 ($K_{sp} = 4 \times 10^{-13}$) in $0.1 \text{ M } K_2CrO_4$ solution will be :-
 (A) 10^{-3} M (B) 10^{-6} M (C) $4 \times 10^{-6} \text{ M}$ (D) $5 \times 10^{-7} \text{ M}$
- Q.72. How many times solubility of CaF_2 is decreased in $4 \times 10^{-3} \text{ M } KF \text{ (aq.)}$ solution as compare to pure water at $25^\circ C$. Given $K_{sp} (CaF_2) = 3.2 \times 10^{-11}$
 (A) 50 (B*) 100 (C) 500 (D) 1000
- Q.73 At $30^\circ C$, In which of the one litre solution, the solubility of Ag_2CO_3 (solubility product = 8×10^{-12}) will be maximum :-
 (A) $0.05 \text{ M } Na_2CO_3$ (B) Pure water (C) $0.05 \text{ M } AgNO_3$ (D) $0.05 \text{ M } NH_3$
- Q.74 What will happen if the pH of the solution of $0.001 \text{ M } Mg(NO_3)_2$ solution is adjusted to $pH = 9$ (K_{sp} of $Mg(OH)_2 = 8.9 \times 10^{-12}$)
 (A) ppt will take place (B) ppt will not take place
 (C) Solution will be saturated (D) None of these
- Q.75 Na_3PO_4 which should be added in 10 L of $1.0 \times 10^{-5} \text{ M } BaCl_2$ solution without any precipitation of $Ba_3(PO_4)_2$ is [K_{sp} of $Ba_3(PO_4)_2 = 4 \times 10^{-23}$]
 (A) $2 \times 10^{-4} \text{ gm}$ (B) 0.328 gm (C) 0.164 gm (D) 0.82 gm

EXERCISE # O-II

Single correct :

- Q.1 The pH of the solution produced when an aqueous solution of strong acid pH 5 is mixed with equal volume of an aqueous solution of strong acid of pH 3 is :-
 (A) 3.3 (B) 3.5 (C) 4.5 (D) 4.0
- Q.2 How many moles of HCl must be removed from 1 litre of aqueous HCl solution to change its pH from 2 to 3 :-
 (A) 1 (B) 0.02 (C) 0.009 (D) 0.01
- Q.3 Which of the following is most soluble in water?
 (A) MnS ($K_{sp} = 8 \times 10^{-37}$) (B) ZnS ($K_{sp} = 7 \times 10^{-16}$)
 (C) Bi_2S_3 ($K_{sp} = 1 \times 10^{-72}$) (D) $\text{Ag}_3(\text{PO}_4)$ ($K_{sp} = 1.8 \times 10^{-18}$)
- Q.4 Solubility of AgBr will be minimum in :-
 (A) Pure water (B) 0.1 M CaBr_2 (C) 0.1 M NaBr (D) 0.1 M AgNO_3
- Q.5 pH of solution at first $1/4^{\text{th}}$ equivalence point of Na_2CO_3 when titrated with HCl will be (for H_2CO_3 $K_{a1} = 10^{-7}$; $K_{a2} = 10^{-11}$)
 (A) $7 + \log 3$ (B) $7 - \log 3$ (C) $11 + \log 3$ (D) $11 - \log 3$
- Q.6 An acid-base indicator has a $K_a = 1.0 \times 10^{-5}$. The acid form of the indicator is red and the basic form is blue. Calculate the pH change required to change the colour of the indicator from 80% red to 80% blue.
 (A) 1.20 (B) 0.80 (C) 0.20 (D) 1.40

Assertion / Reason :

- Q.7 **Statement-1** pH of 10^{-7} M NaOH solution is exist between 7 to 7.3 at 25°C .
Statement-2 Due to common ion effect ionization of water is reduced.
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
 (C) Statement-1 is true, statement-2 is false.
 (D) Statement-1 is false, statement-2 is true.
- Q.8 **Statement-1** In general phenolphthalein is used as an indicator for the titration of weak acid (HA) against strong base (NaOH)
Statement-2 At equivalent point solution is basic.
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
 (C) Statement-1 is true, statement-2 is false.
 (D) Statement-1 is false, statement-2 is true.
- Q.9 **Statement-1** : Moles of Sr^{2+} furnished by sparingly soluble substance $\text{Sr}(\text{OH})_2$ decreases due to dilution.
Statement-2 : Solubility product constant of $\text{Sr}(\text{OH})_2$ is not affected by dilution.
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
 (C) Statement-1 is true, statement-2 is false.
 (D) Statement-1 is false, statement-2 is true.

- Q.10 **Statement-1** : On dilution of a concentrated solution of CH_3COOH , the concentration of $[\text{H}^+]$ decreases.
Statement-2 : Increase in volume is more than the increase in degree of ionisation.
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
 (C) Statement-1 is true, statement-2 is false.
 (D) Statement-1 is false, statement-2 is true.

Multiple correct :

- Q.11 Which of the following is correct for 0.1 M BOH solution ($K_b = 10^{-5}$)
 (A) pH of solution is 11
 (B) OH^- concentration is 10^{-3} mol/L
 (C) its salt with HCl (i.e. BCl) form the acidic solution in water
 (D) Phenolphthalein indicator can be used during the titration of BOH with HCl
- Q.12 For weak monobasic acid, HA, the dissociation constant is 2×10^{-6} , at 25°C . Which of the following is/are correct regarding this acid? [$\log 2 = 0.3$]
 (A) $\text{A}^- + \text{H}_2\text{O} \rightleftharpoons \text{HA} + \text{OH}^-$; $K_{\text{eq}} = 5 \times 10^{-9}$
 (B) The equilibrium constant for the reaction of HA with aq. NaOH is 2×10^8
 (C) The pH of 0.1 M, HA solution is 3.35
 (D) solution of A^- is basic
- Q.13 Select correct statement for 50ml 0.1M $\text{H}_2\text{A}(\text{aq.})$ solution ; $K_{a_1} = 10^{-5}$; $K_{a_2} = 10^{-8}$
 (A) $[\text{H}^+] = 2[\text{A}^{2-}]$
 (B) pH of 0.1M H_2A solution is 3
 (C) In above H_2A solution when 5 millimoles of NaHA are added then pH increases by 2 units
 (D) 50 ml of 0.1M NaOH required to neutralised completely 50 ml of 0.1M H_2A solution
- Q.14 A solution containing 0.01M each of Pb^{2+} , Ag^+ , Zn^{2+} & Cr^{3+} ion. If solid Na_2S is added slowly to the solution then correct statement is based on given data -

Precipitate	PbS	Ag_2S	ZnS	Cr_2S_3
K _{sp}	10^{-11}	10^{-12}	10^{-8}	10^{-10}

- (A) Pb^{2+} will start precipitating first
 (B) Cr^{3+} will start precipitating last
 (C) Zn^{2+} will start precipitating before Ag^+
 (D) When Zn^{2+} just starts precipitating then Pb^{2+} ion gets 99.9% precipitated
- Q.15 If K_1 & K_2 be first and second ionisation constant of H_3PO_4 and $K_1 \gg K_2$ which is/are incorrect.
 (A) $[\text{H}^+] = [\text{H}_2\text{PO}_4^-]$ (B) $[\text{H}^+] = \sqrt{K_1[\text{H}_3\text{PO}_4]}$
 (C) $K_2 = [\text{HPO}_4^{2-}]$ (D) $[\text{H}^+] = 3[\text{PO}_4^{3-}]$
- Q.16 10 ml. of a solution contains 0.1 M NH_4Cl + 0.01M NH_4OH . Which addition would not change the pH of solution :-
 (A) Adding 1 ml. water (B) Adding 5 ml. of 0.1 M NH_4Cl
 (C) Adding 5 ml. of 0.1 M NH_4OH (D) Adding 10 ml. of 0.1 M NH_4Cl

- Q.17 When equal volumes of the following solutions are mixed, precipitation of AgCl ($K_{sp} = 1.8 \times 10^{-10}$) will occur only with:
- (A) $10^{-4} \text{ M (Ag}^+) \text{ and } 10^{-4} \text{ M (Cl}^-)$ (B) $10^{-5} \text{ M (Ag}^+) \text{ and } 10^{-5} \text{ M (Cl}^-)$
 (C) $10^{-6} \text{ M (Ag}^+) \text{ and } 10^{-6} \text{ M (Cl}^-)$ (D) $10^{-10} \text{ M (Ag}^+) \text{ and } 10^{-10} \text{ M (Cl}^-)$

Paragraph for Q.18 to Q.20

8 gm weak acid HX (molecular mass = 80) is dissolved in 100 ml water. ($K_a = 10^{-4}$)

- Q.18 Find pH of solution-
 (A) 3.3 (B) 2 (C) 2.3 (D) 3
- Q.19 If it is titrated with 0.25 M NaOH find pH at equivalence point ($\log 5 = 0.7$)
 (A) 9.15 (B) 8.65 (C) 4.65 (D) 4.85
- Q.20 Find $[\text{H}^+]$ if 10^{-3} mol HCl is added to 100 ml original solution ($\sqrt{41} = 6.4$; $\sqrt{5} = 2.24$)
 (A) 0.62×10^{-2} (B) 1.62×10^{-2} (C) 2.7×10^{-2} (D) 0.27×10^{-2}

MATCH THE COLUMN :

- Q.21 Match the effect of addition of 1 M NaOH to 100 mL 1 M CH_3COOH (in Column I) with pH (in Column II):

Column-I

- (A) 25 mL of NaOH
 (B) 50 mL of NaOH
 (C) 75 mL of NaOH
 (D) 100 mL of NaOH

Column-II

- (P) pK_a
 (Q) $\text{pK}_a + \log 3$
 (R) $\text{pK}_a - \log 3$
 (S) $\frac{1}{2} [\text{pK}_w + \text{pK}_a - \log 2]$

- Q.22 **Column-I**
PH

- (A) 3
 (B) 5
 (C) 8
 (D) 9

Column-II
Solution

- (P) When equal volumes of 0.2M NH_4OH ($K_b = 10^{-5}$) & 0.2M HCl are mixed
 (Q) When equal volumes of 0.2M CH_3COONa & 0.2M HCl are mixed ($K_{a(\text{CH}_3\text{COOH})} = 10^{-5}$)
 (R) 0.1M Na_2HPO_4
 (for H_3PO_4 ; $K_{a1} = 10^{-4}$; $K_{a2} = 10^{-6}$; $K_{a3} = 10^{-10}$)
 (S) At 1st half equivalence point of H_2CO_3 when titrated against 0.1M NaOH , $K_{a1} = 10^{-5}$, $K_{a2} = 10^{-9}$
 (T) Mg(OH)_2 ; $K_{sp} = 5 \times 10^{-16}$

TABLE TYPE QUESTION :

Column-I (solution)	Column-II (pH of solution)	Column-III (Introduction about solution)
(A) $\text{CH}_3\text{COOH}(0.2\text{M}, 1\text{L}) + \text{NaOH}(0.1\text{M}, 1\text{L})$	(P) 1.3	(1) pH is determined by strong acid
(B) $\text{CH}_3\text{COOH}(0.1\text{M}, 1\text{L}) + \text{HCl}(0.1\text{M}, 1\text{L})$	(Q) 7	(2) Buffer solution at its maximum buffer capacity
(C) $\text{CH}_3\text{COOH}(0.1\text{M}, 1\text{L}) + \text{NH}_4\text{OH}(0.1\text{M}, 1\text{L})$	(R) 9	(3) pH is determined by salt hydrolysis.
(D) $\text{NH}_4\text{Cl}(200\text{ ml}, 0.1\text{M}) + \text{NaOH}(100\text{ ml}, 0.1\text{M})$	(S) 5	(4) pH is determined by buffer solution

(Given : $(K_a)_{\text{CH}_3\text{COOH}} = 10^{-5}$, $(K_b)_{\text{NH}_4\text{OH}} = 10^{-5}$)

Q.23 Which of the following is incorrectly matched

- (A) A - S - 4 (B) B - P - 1 (C) D - R - 2 (D) C - Q - 1

Q.24 If 0.15 mole NaOH is added in solution (B) of column-I then which of the following is correct

- (A) S - 3 (B) S - 4 (C) R - 1 (D) P - 3

Q.25 If 0.1mole HCl is added in solution (A) of column-I then pH of the resulting solution will be

- (A) 7 (B) 13 (C) 3.0 (D) 1

EXERCISE # J-MAIN

- Q.1 The solubility in water of a sparingly soluble salt AB_2 is $1.0 \times 10^{-5} \text{ mol L}^{-1}$. Its solubility product will be [AIEEE-2003]
 (1) 1×10^{-15} (2) 1×10^{-10} (3) 4×10^{-15} (4) 4×10^{-10}
- Q.2 The solubility of $Mg(OH)_2$ is x mole/lit. then its solubility product is- [AIEEE-2002]
 (1) x^3 (2) $5x^3$ (3) $4x^3$ (4) $2x^2$
- Q.3 The molar solubility in mol L^{-1} of a sparingly soluble salt MX_4 is 's'. The corresponding solubility product is K_{sp} . 's' is given in terms of K_{sp} by relation : [AIEEE-2004]
 (1) $s = (K_{sp} / 128)^{1/4}$ (2) $s = (128K_{sp})^{1/4}$
 (3) $s = (256K_{sp})^{1/5}$ (4) $s = (K_{sp}/256)^{1/5}$
- Q.4 The solubility product of a salt having general formula MX_2 , in water is : 4×10^{-12} . The concentration of M^{2+} ions in the aqueous solution of the salt is - [AIEEE-2005]
 (1) $1.0 \times 10^{-4} \text{ M}$ (2) $2.0 \times 10^{-6} \text{ M}$ (3) $4.0 \times 10^{-10} \text{ M}$ (4) $1.6 \times 10^{-4} \text{ M}$
- Q.5 Hydrogen ion concentration in mol/L in a solution of $\text{pH} = 5.4$ will be - [AIEEE-2005]
 (1) 3.88×10^6 (2) 3.98×10^8 (3) 3.98×10^{-6} (4) 3.68×10^{-6}
- Q.6 In a saturated solution of the sparingly soluble strong electrolyte $AgIO_3$ (molecular mass = 283) the equilibrium which sets in is - [AIEEE-2007]

$$AgIO_3 \rightleftharpoons Ag^+_{(aq)} + IO_3^-_{(aq)}$$

 If the solubility product constant K_{sp} of $AgIO_3$ at a given temperature is 1.0×10^{-8} , what is the mass of $AgIO_3$ contained in 100 ml of its saturated solution ?
 (1) $28.3 \times 10^{-2} \text{ g}$ (2) $2.83 \times 10^{-3} \text{ g}$ (3) $1.0 \times 10^{-7} \text{ g}$ (4) $1.0 \times 10^{-4} \text{ g}$
- Q.7 The pK_a of a weak acid, HA, is 4.80. The pK_b of a weak base, BOH, is 4.78. The pH of an aqueous solution of the corresponding salt, BA, will be - [AIEEE-2008]
 (1) 9.58 (2) 4.79 (3) 7.01 (4) 9.22
- Q.8 Solid $Ba(NO_3)_2$ is gradually dissolved in a $1.0 \times 10^{-4} \text{ M Na}_2\text{CO}_3$ solution. At what concentration of Ba^{2+} will a precipitate begin to form? [AIEEE-2009]
 (K_{sp} for $BaCO_3 = 5.1 \times 10^{-9}$)
 (1) $8.1 \times 10^{-8} \text{ M}$ (2) $8.1 \times 10^{-7} \text{ M}$ (3) $4.1 \times 10^{-5} \text{ M}$ (4) $5.1 \times 10^{-5} \text{ M}$
- Q.9 Solubility product of silver bromide is 5.0×10^{-13} . The quantity of potassium bromide (molar mass taken as 120 g mol^{-1}) to be added to 1 litre of 0.05 M solution of silver nitrate to start the precipitation of AgBr is :- [AIEEE-2010]
 (1) $5.0 \times 10^{-8} \text{ g}$ (2) $1.2 \times 10^{-10} \text{ g}$ (3) $1.2 \times 10^{-9} \text{ g}$ (4) $6.2 \times 10^{-5} \text{ g}$
- Q.10 In aqueous solution the ionization constants for carbonic acid are
 $K_1 = 4.2 \times 10^{-7}$ and $K_2 = 4.8 \times 10^{-11}$ [AIEEE-2010]
 Select the correct statement for a saturated 0.034 M solution of the carbonic acid :-
 (1) The concentration of H^+ is double that of CO_3^{2-}
 (2) The concentration of CO_3^{2-} is 0.034 M
 (3) The concentration of CO_3^{2-} is greater than that of HCO_3^-
 (4) The concentrations of H^+ and HCO_3^- are approximately equal

Q.11 At 25° C, the solubility product of $\text{Mg}(\text{OH})_2$ is 1.0×10^{-11} . At which pH, will Mg^{2+} ions start precipitating in the form of $\text{Mg}(\text{OH})_2$ from a solution of 0.001 M Mg^{2+} ions ? [AIEEE–2010]

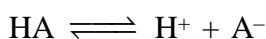
- (1) 8 (2) 9 (3) 10 (4) 11

Q.12 The K_{sp} for $\text{Cr}(\text{OH})_3$ is 1.6×10^{-30} . The molar solubility of this compound in water is :-

[AIEEE–2011]

- (1) $\sqrt[3]{1.6 \times 10^{-30}}$ (2) $\sqrt[4]{1.6 \times 10^{-30}}$ (3) $\sqrt[4]{1.6 \times 10^{-30} / 27}$ (4) $1.6 \times 10^{-30} / 27$

Q.13 An acid HA ionises as



The pH of 1.0 M solution is 5. Its dissociation constant would be :-

[AIEEE–2011]

- (1) 1×10^{-10} (2) 5 (3) 5×10^{-8} (4) 1×10^{-5}

Q.14 If K_{sp} of CaF_2 at 25°C is 1.7×10^{-10} , the combination amongst the following which gives a precipitate of CaF_2 is :- [JEE-MAIN(online)–2012]

- (1) 1×10^{-2} M Ca^{2+} and 1×10^{-5} M F^- (2) 1×10^{-4} M Ca^{2+} and 1×10^{-4} M F^-
(3) 1×10^{-3} M Ca^{2+} and 1×10^{-5} M F^- (4) 1×10^{-2} M Ca^{2+} and 1×10^{-3} M F^-

Q.15 The pH of a 0.1 molar solution of the acid HQ is 3. The value of the ionization constant, K_a of this acid is :- [AIEEE–2012]

- (1) 1×10^{-7} (2) 3×10^{-7} (3) 1×10^{-3} (4) 1×10^{-5}

Q.16 How many litres of water must be added to 1 litre of an aqueous solution of HCl with a pH of 1 to create an aqueous solution with pH of 2 ? [AIEEE–2013]

- (1) 0.1 L (2) 0.9 L (3) 2.0 L (4) 9.0 L

Q.17 Solid $\text{Ba}(\text{NO}_3)_2$ is gradually dissolved in a 1.0×10^{-4} M Na_2CO_3 solution. At which concentration of Ba^{2+} , precipitate of BaCO_3 begins to form ? (K_{sp} for $\text{BaCO}_3 = 5.1 \times 10^{-9}$)

- (1) 5.1×10^{-5} M (2) 8.1×10^{-7} M [JEE-MAIN(Online)–2013]
(3) 4.1×10^{-5} M (4) 7.1×10^{-8} M

Q.18 NaOH is a strong base. What will be pH of 5.0×10^{-2} M NaOH solution ? ($\log 2 = 0.3$)

[JEE-MAIN(Online)–2013]

- (1) 13.70 (2) 13.00 (3) 14.00 (4) 12.70

Q.19 Which one of the following arrangements represents the correct order of solubilities of sparingly soluble salts Hg_2Cl_2 , $\text{Cr}_2(\text{SO}_4)_3$, BaSO_4 and CrCl_3 respectively ? [JEE-MAIN(Online)–2013]

- (1) $\left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}}$, $\left(\frac{K_{sp}}{108}\right)^{\frac{1}{5}}$, $(K_{sp})^{\frac{1}{2}}$, $\left(\frac{K_{sp}}{27}\right)^{\frac{1}{4}}$ (2) $(K_{sp})^{\frac{1}{2}}$, $\left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}}$, $\left(\frac{K_{sp}}{27}\right)^{\frac{1}{4}}$, $\left(\frac{K_{sp}}{108}\right)^{\frac{1}{5}}$
(3) $(K_{sp})^{\frac{1}{2}}$, $\left(\frac{K_{sp}}{108}\right)^{\frac{1}{5}}$, $\left(\frac{K_{sp}}{27}\right)^{\frac{1}{4}}$, $\left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}}$ (4) $\left(\frac{K_{sp}}{108}\right)^{\frac{1}{5}}$, $\left(\frac{K_{sp}}{27}\right)^{\frac{1}{4}}$, $(K_{sp})^{\frac{1}{2}}$, $\left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}}$

Q.20 What would be the pH of a solution obtained by mixing 5 g of acetic acid and 7.5 g of sodium acetate and making the volume equal to 500 mL? [JEE-MAIN(Online)–2013]

($K_a = 1.75 \times 10^{-5}$, $pK_a = 4.76$)

- (1) $4.76 < \text{pH} < 5.0$
- (2) $\text{pH} < 4.70$
- (3) pH of solution will be equal to pH of acetic acid
- (4) $\text{pH} = 4.70$

Q.21 In some solutions, the concentration of H_3O^+ remains constant even when small amounts of strong acid or strong base are added to them. These solutions are known as :-[JEE-MAIN(Online)–2014]

- (1) Colloidal solutions
- (2) True solutions
- (3) Ideal solutions
- (4) Buffer solutions

Q.22 Zirconium phosphate $[\text{Zr}_3(\text{PO}_4)_4]$ dissociates into three zirconium cations of charge +4 and four phosphate anions of charge –3. If molar solubility of zirconium phosphate is denoted by S and its solubility product by K_{sp} then which of the following relationship between S and K_{sp} is correct ?

- (1) $S = \{K_{sp}/144\}^{1/7}$
- (2) $S = \{K_{sp}/(6912)^{1/7}\}$ [JEE-MAIN(Online)–2014]
- (3) $S = (K_{sp}/6912)^{1/7}$
- (4) $S = \{K_{sp}/6912\}^{1/7}$

Q.23 pK_a of a weak acid (HA) and pK_b of a weak base (BOH) are 3.2 and 3.4, respectively. The pH of their salt (AB) solution is [JEE-MAIN(Offline)–2017]

- (1) 7.2
- (2) 6.9
- (3) 7.0
- (4) 1.0

Q.24 Addition of sodium hydroxide solution to a weak acid (HA) results in a buffer of pH 6. If ionisation constant of HA is 10^{-5} , the ratio of salt to acid concentration in the buffer solution will be :

[JEE-MAIN(Online)–2017]

- (1) 4 : 5
- (2) 1 : 10
- (3) 10 : 1
- (4) 5 : 4

Q.25 50 mL of 0.2 M ammonia solution is treated with 25 mL of 0.2 M HCl. If pK_b of ammonia solution is 4.75, the pH of the mixture will be:- [JEE-MAIN(Online)–2017]

- (1) 8.25
- (2) 4.75
- (3) 9.25
- (4) 3.75

Q.26 Which of the following salts is the most basic in aqueous solution ? [JEE-MAIN(Offline)–2018]

- (1) CH_3COOK
- (2) FeCl_3
- (3) $\text{Pb}(\text{CH}_3\text{COO})_2$
- (4) $\text{Al}(\text{CN})_3$

Q.27 An alkali is titrated against an acid with methyl orange as indicator, which of the following is a correct combination ?

[JEE-MAIN(Offline)–2018]

- | Base | Acid | End point |
|------------|--------|-----------------------|
| (1) Strong | Strong | Pinkish red to yellow |
| (2) Weak | Strong | Yellow to pinkish red |
| (3) Strong | Strong | Pink to colourless |
| (4) Weak | Strong | Colourless to pink |

Q.28 An aqueous solution contains 0.10 M H_2S and 0.20 M HCl. If the equilibrium constants for the formation of HS^- from H_2S is 1.0×10^{-7} and that of S^{2-} from HS^- ions is 1.2×10^{-13} then the concentration of S^{2-} ions in aqueous solution is : [JEE-MAIN(Offline)–2018]

- (1) 3×10^{-20}
- (2) 6×10^{-21}
- (3) 5×10^{-19}
- (4) 5×10^{-8}

Q.29 A aqueous solution contains an unknown concentration of Ba^{2+} . When 50 mL of a 1 M solution of Na_2SO_4 is added, BaSO_4 just begins to precipitate. The final volume is 500 mL. The solubility product of BaSO_4 is 1×10^{-10} . What is the original concentration of Ba^{2+} ? [JEE-MAIN(Offline)-2018]

- (1) $2 \times 10^{-9} \text{ M}$ (2) $1.1 \times 10^{-9} \text{ M}$ (3) $1.0 \times 10^{-10} \text{ M}$ (4) $5 \times 10^{-9} \text{ M}$

Q.30 Following four solutions are prepared by mixing different volumes of NaOH and HCl of different concentrations, pH of which one of them will be equal to 1? [JEE-MAIN(Online)-2018]

- (1) $75\text{mL} \frac{\text{M}}{5} \text{HCl} + 25\text{mL} \frac{\text{M}}{5} \text{NaOH}$ (2) $100\text{mL} \frac{\text{M}}{10} \text{HCl} + 100\text{mL} \frac{\text{M}}{10} \text{NaOH}$

- (3) $55\text{mL} \frac{\text{M}}{10} \text{HCl} + 45\text{mL} \frac{\text{M}}{10} \text{NaOH}$ (4) $60\text{mL} \frac{\text{M}}{10} \text{HCl} + 40\text{mL} \frac{\text{M}}{10} \text{NaOH}$

Q.31 The minimum volume of water required to dissolve 0.1 g lead (II) chloride to get a saturated solution (K_{sp} of $\text{PbCl}_2 = 3.2 \times 10^{-8}$; atomic mass of Pb = 207 u) is : [JEE-MAIN(Online)-2018]

- (1) 0.36 L (2) 0.18 L (3) 17.98 L (4) 1.798 L

EXERCISE # J-ADVANCE

- Q.1 What will be the resultant pH when 200 ml of an aqueous solution of HCl (pH = 2.0) is mixed with 300 ml of an aqueous solution of NaOH (pH = 12.0) ? [JEE '1998]
- Q.2 The pH of 0.1 M solution of the following salts increases in the order [JEE 1999]
 (A) $\text{NaCl} < \text{NH}_4\text{Cl} < \text{NaCN} < \text{HCl}$
 (B) $\text{HCl} < \text{NH}_4\text{Cl} < \text{NaCl} < \text{NaCN}$
 (C) $\text{NaCN} < \text{NH}_4\text{Cl} < \text{NaCl} < \text{HCl}$
 (D) $\text{HCl} < \text{NaCl} < \text{NaCN} < \text{NH}_4\text{Cl}$
- Q.3 A buffer solution can be prepared from a mixture of [JEE 1999]
 (A) sodium acetate and acetic acid in water
 (B) sodium acetate and hydrochloric acid in water
 (C) ammonia and ammonium chloride in water
 (D) ammonia and sodium hydroxide in water.
- Q.4 The solubility of $\text{Pb}(\text{OH})_2$ in water is $6.7 \times 10^{-6} \text{ M}$. Calculate the solubility of $\text{Pb}(\text{OH})_2$ in a buffer solution of pH = 8. [JEE '1999]
- Q.5 The average concentration of SO_2 in the atmosphere over a city on a certain day is 10 ppm, when the average temperature is 298 K. Given that the solubility of SO_2 in water at 298 K is 1.3653 moles litre^{-1} and the pK_a of H_2SO_3 is 1.92, estimate the pH of rain on that day. [JEE 2000]
 [Given : $10^{-1.92} = 1.2 \times 10^{-2}$, $\sqrt{5.5678} = 2.5627$, $\log(1.2213) = 0.0868$]
- Q.6 For sparingly soluble salt ApBq , the relationship of its solubility product (L_s) with its solubility (S) is - [JEE 2001]
 (A) $L_s = S^{p+q}$, p^p , q^q (B) $L_s = S^{p+q}$, p^p , q^p
 (C) $L_s = S^{pq}$, p^p , q^q (D) $L_s = S^{pq}$, $(p.q)^{p+q}$
- Q.7 500 ml of 0.2 M aqueous solution of acetic acid is mixed with 500 mL of 0.2 M HCl at 25°C.
 (a) Calculate the degree of dissociation of acetic acid in the resulting solution and pH of the solution.
 (b) If 6 g of NaOH is added to the above solution, determine final pH. Assume there is no change in volume on mixing. K_a of acetic acid is $1.75 \times 10^{-5} \text{ M}$. [JEE 2002]
- Q.8 A solution which is 10^{-3} M each in Mn^{2+} , Fe^{2+} , Zn^{2+} and Hg^{2+} is treated with 10^{-16} M sulphide ion. If K_{sp} , MnS , FeS , ZnS and HgS are 10^{-15} , 10^{-23} , 10^{-20} and 10^{-54} respectively, which one will precipitate first ? [JEE 2003]
 (A) FeS (B) MnS (C) HgS (D) ZnS
- Q.9 Will the pH of water be same at 4°C and 25°C ? Explain. [JEE 2003]

- Q.10 0.1 M of HA is titrated with 0.1 M NaOH, calculate the pH at end point. Given $K_a(\text{HA}) = 5 \times 10^{-6}$ and $\alpha \ll 1$. [JEE 2004]
- Q.11 HX is a weak acid ($K_a = 10^{-5}$). It forms a salt NaX (0.1 M) on reacting with caustic soda. The degree of hydrolysis of NaX is
(A) 0.01% (B) 0.0001% (C) 0.1% (D) 0.5% [JEE 2004]
- Q.12 CH_3NH_2 (0.1 mole, $K_b = 5 \times 10^{-4}$) is added to 0.08 moles of HCl and the solution is diluted to one litre, resulting hydrogen ion concentration is
(A) 1.6×10^{-11} (B) 8×10^{-11} (C) 5×10^{-5} (D) 2×10^{-2} [JEE 2005]
- Q.13 If $\text{Ag}^+ + \text{NH}_3 \rightleftharpoons [\text{Ag}(\text{NH}_3)]^+$; $K_1 = 1.6 \times 10^3$ and
 $[\text{Ag}(\text{NH}_3)]^+ + \text{NH}_3 \rightleftharpoons [\text{Ag}(\text{NH}_3)_2]^+$; $K_2 = 6.8 \times 10^3$.
The formation constant of $[\text{Ag}(\text{NH}_3)_2]^+$ is :
(A) 6.08×10^{-6} (B) 6.8×10^{-6} (C) 1.6×10^3 (D) 1.088×10^7 [JEE 2006]
- Q.14 The species present in solution when CO_2 is dissolved in water :
(A) CO_2 , H_2CO_3 , HCO_3^- , CO_3^{2-} (B) H_2CO_3 , CO_3^{2-} [JEE 2006]
(C) CO_3^{2-} , HCO_3^- (D) CO_2 , H_2CO_3
- Q.15 2.5 mL of $\frac{2}{5}$ M weak monoacidic base ($K_b = 1 \times 10^{-12}$ at 25°C) is titrated with $\frac{2}{15}$ M HCl in water at 25°C . The concentration of H^+ at equivalence point is [JEE 2008]
($K_w = 1 \times 10^{-14}$ at 25°C)
(A) 3.7×10^{-13} M (B) 3.2×10^{-7} M
(C) 3.2×10^{-2} M (D) 2.7×10^{-2} M
- Q.16 Solubility product constants (K_{sp}) of salts of types MX, MX_2 and M_3X at temperature 'T' are 4.0×10^{-8} , 3.2×10^{-14} and 2.7×10^{-15} , respectively. Solubilities (mol dm^{-3}) of the salts at temperature 'T' are in the order :
(A) $\text{MX} > \text{MX}_2 > \text{M}_3\text{X}$ (B) $\text{M}_3\text{X} > \text{MX}_2 > \text{MX}$ [JEE 2008]
(C) $\text{MX}_2 > \text{M}_3\text{X} > \text{MX}$ (D) $\text{MX} > \text{M}_3\text{X} > \text{MX}_2$
- Q.17 The dissociation constant of a substituted benzoic acid at 25°C is 1.0×10^{-4} . The pH of a 0.01 M solution of its sodium salt is [JEE 2009]
- Q.18 Aqueous solutions of HNO_3 , KOH, CH_3COOH and CH_3COONa of identical concentrations are provided. The pair(s) of solutions which form a buffer upon mixing is(are) –
(A) HNO_3 and CH_3COOH
(B) KOH and CH_3COONa
(C) HNO_3 and CH_3COONa
(D) CH_3COOH and CH_3COONa

- Q.19 In 1 L saturated solution of AgCl [$K_{sp}(\text{AgCl}) = 1.6 \times 10^{-10}$], 0.1 mol of CuCl [$K_{sp}(\text{CuCl}) = 1.0 \times 10^{-6}$] is added. The resultant concentration of Ag^+ in the solution is 1.6×10^{-x} . The value of 'x' is. **[JEE -2011]**
- Q.20 The K_{sp} of Ag_2CrO_4 is 1.1×10^{-12} at 298 K. The solubility (in mol/L) of Ag_2CrO_4 in a 0.1 M AgNO_3 solution is **[JEE 2013]**
- (A) 1.1×10^{-11} (B) 1.1×10^{-10}
(C) 1.1×10^{-12} (D) 1.1×10^{-9}
- Q.21 The solubility of a salt of weak acid (AB) at pH 3 is $Y \times 10^{-3} \text{ mol L}^{-1}$. The value of Y is ____.
(Given that the value of solubility product of AB (K_{sp}) = 2×10^{-10} and the value of ionization constant of HB (K_a) = 1×10^{-8}) **[JEE 2018]**

ANSWER KEY

EXERCISE # S-I

- Q.1 Ans. 6.022×10^7 Q.2 Ans. (i) 6.53 ; (ii) (a) Basic , (b) Acidic
- Q.3 Ans. 6.8
- Q.4 Ans. (a) 1, (b) 2.87, (c) 11.13 (d) 6.97, (e) 7, (f) 6, (g) 6.97, (h) 11.30 (i) 9, (j) 3
- Q.5 Ans. (a) $K_a = 10^{-8}$, (b) $K_b = 10^{-6}$ Q.6 Ans. 10
- Q.7 Ans. 173.2 : 1 Q.8 Ans. 0.009
- Q.9 Ans. 2.32×10^{-8} M Q.10 Ans. 1.1×10^{-3} M
- Q.11 Ans. 1.11×10^{-4} Q.12 Ans. 4.7
- Q.13 Ans. 3.3 Q.14 Ans. (a) 0.522 , (b) 2.522
- Q.15. Ans. (1)
- Q.16 Ans. $[H^+] = 1.65 \times 10^{-2}$ M, $[CHCl_2COO^-] = 6.5 \times 10^{-3}$ M
- Q.17 Ans. $[H^+] = 10^{-3}$ M, $[CH_3COO^-] = 3.6 \times 10^{-4}$ M, $[C_7H_5O_2^-] = 6.4 \times 10^{-4}$ M
- Q.18 Ans. 0.027 M, 0.073 M, 0.027 M, 10^{-5} M
- Q.19 Ans. $[H^+] = [H_2PO_4^-] = 2.7 \times 10^{-3}$ M, $[HPO_4^{2-}] = 10^{-8}$ M, $[PO_4^{3-}] = 3.7 \times 10^{-19}$ M
- Q.20 Ans. 11.3 Q.21 Ans. 10^{-5} M
- Q.22 Ans. pH = 4.5 Q.23 Ans. $K_b = 6.25 \times 10^{-10}$
- Q.24 Ans. 0.56%, pH = 7 Q.25 Ans. 1.667%
- Q.26 Ans. 0.25 % Q.27 Ans. 10^{-6} ; 10^{-8}
- Q.28 Ans. 8.3 Q.29 Ans. 4.19
- Q.30 Ans. (a) 6, (b) 1×10^{-5} Q.31 Ans. 9.0
- Q.32 Ans. 9.56 Q.33 Ans. 5.04
- Q.34 Ans. 0.05 mol Q.35 Ans. $[OH^-] = 9.0 \times 10^{-6}$ M
- Q.36 Ans. (10.1) Q.37 Ans. 4.74
- Q.38 Ans. 9.56 Q.39 Ans. 8.7782
- Q.40 Ans. (3.33) Q.41 Ans. 10^{-5} M
- Q.42 Ans. 8.7, $[H_3O^+] = 2 \times 10^{-9}$ M Q.43 Ans. 5, 10^{-5} M
- Q.44 Ans. (i) 2.85, (ii) 4.0969, (iii) 4.5229, (iv) 4.699, (v) 5.301, (vi) 8.699
- Q.45 Ans. $[HI_n] = 80$ % Q.46 Ans. 85.71%
- Q.47 Ans. (b), (c) Q.48 Ans. $\Delta pH = 0.954$
- Q.49 Ans. QX_2 is more soluble Q.50 Ans. 4×10^{-8}
- Q.51 Ans. 5×10^{-11} Q.52 Ans. 3.2×10^{-11}
- Q.53 Ans. 2.56×10^{-16} Q.54 Ans. 1.0×10^{-5} mol/lit
- Q.55 Ans. 5×10^{-10} M
- Q.56 Ans. 5×10^{-7}
- Q.57 Ans. 4×10^{-7} mol/L AgBr, 1.6×10^{-6} mol/L AgSCN
- Q.58 Ans. $[F^-] = 3 \times 10^{-3}$ M Q.59 Ans. 8×10^{-3} M
- Q.60 Ans. (i) 2×10^{-9} , (ii) 8×10^{-3} Q.61 Ans. $S = 2 \times 10^{-4}$ M, pH = 8.0
- Q.62 Ans. 4×10^{-2} M

Q.63 Ans. (a) no precipitation will occur, (b) a precipitate will form

Q.64 Ans. No.

Q.65 Ans. 0.284 gm

EXERCISE # S-II

Q.1 Ans. 0.209 M, 0.191 M, 9.13×10^{-3} M, 0 Q.2 Ans. pH = 11.48, $[\text{enH}_2^{2+}] = 7.1 \times 10^{-8}$ M

Q.3 Ans. 10.6

Q.4 Ans. $[\text{S}^{2-}] = 2.5 \times 10^{-15}$ M

Q.5 Ans. (2×10^{-4}) M

Q.6 Ans. pH = 10.52

Q.7 Ans. $[\text{OH}^-] = 3.73 \times 10^{-2}$ M, $[\text{H}_3\text{PO}_4] = 6 \times 10^{-18}$ M

Q.8 Ans. 8.35, 9.60, 4.66

Q.9 Ans. (9.6)

Q.10 Ans. $K_b \approx 1.73 \times 10^{-5}$, 5.27

Q.11 Ans. $K_a \approx 1.73 \times 10^{-5}$, 8.73

Q.12 Ans. (10^{-5}) M

Q.13 Ans. (10^{-3}) M

Q.14 Ans. pH = 7.9, pH = 7.3

Q.15 Ans. 2.8×10^{-3} mole

Q.16 Ans. 1.6×10^{-3}

Q.17 Ans. $K_d = 1/K_f = 4.8 \times 10^{-4}$

EXERCISE # O-I

Q.1 Ans. (A)

Q.2 Ans. (B)

Q.3 Ans. (C)

Q.4 Ans. (C)

Q.5 Ans. (B)

Q.6 Ans. (C)

Q.7 Ans. (D)

Q.8 Ans. (D)

Q.9 Ans. (C)

Q.10 Ans. (C)

Q.11 Ans. (C)

Q.12 Ans. (D)

Q.13 Ans. (B)

Q.14 Ans. (B)

Q.15 Ans. (C)

Q.16 Ans. (C)

Q.17 Ans. (B)

Q.18 Ans. (C)

Q.19 Ans. (C)

Q.20 Ans. (B)

Q.21 Ans. (B)

Q.22 Ans. (D)

Q.23 Ans. (D)

Q.24 Ans. (C)

Q.25 Ans. (C)

Q.26 Ans. (C)

Q.27 Ans. (B)

Q.28 Ans. (B)

Q.29 Ans. (A)

Q.30 Ans. (D)

Q.31 Ans. (B)

Q.32 Ans. (C)

Q.33 Ans. (C)

Q.34 Ans. (C)

Q.35 Ans. (B)

Q.36 Ans. (C)

Q.37 Ans. (D)

Q.38 Ans. (A)

Q.39 Ans. (C)

Q.40 Ans. (C)

Q.41 Ans. (C)

Q.42 Ans. (B)

Q.43 Ans. (C)

Q.44 Ans. (D)

Q.45 Ans. (A)

Q.46 Ans. (B)

Q.47 Ans. (D)

Q.48 Ans. (B)

Q.49 Ans. (C)

Q.50 Ans. (A)

Q.51 Ans. (C)

Q.52 Ans. (A)

Q.53 Ans. (A)

Q.54 Ans. (A)

Q.55 Ans. (B)

Q.56 Ans. (D)

Q.57 Ans. (A)

Q.58 Ans. (A)

Q.59 Ans. (B)

Q.60 Ans. (C)

Q.61 Ans. (D)

Q.62 Ans. (A)

Q.63 Ans. (D)

Q.64 Ans. (C)

Q.65 Ans. (D)

Q.66 Ans. (D)

Q.67 Ans. (D)

Q.68 Ans. (C)

Q.69 Ans. (A)

Q.70 Sol. (C)

Q.71 Ans. (B)

Q.72 Ans. (B)

Q.73 Ans. (D)

Q.74 Ans. (B)

Q.75 Ans. (B)

EXERCISE # O-II

Q.1 Ans.(A)	Q.2 Ans.(C)	Q.3 Ans.(D)
Q.4 Ans.(B)	Q.5 Ans (C)	Q.6 Ans.(A)
Q.7 Ans.(A)	Q.8 Ans.(B)	Q.9 Ans.(D)
Q.10 Ans.(A)	Q.11 Ans. (A,B,C)	Q.12 Ans.(A,B,C,D)
Q.13 Ans.(B,C)	Q.14 Ans. (A, B, D)	Q.15 Ans. (D)
Q.16 Ans.(A)	Q.17 Ans. (A)	Q.18 Ans (B)
Q.19 Ans (B)	Q.20 Ans (B)	
Q.21 Ans. A - (R), B - (P), C - (Q), D - (S)		
Q.22 Ans (A) - Q; (B) - P, S; (C) - R; (D) - T		
Q.23 Ans.(D)	Q.24 Ans.(B)	Q.25 Ans.(C)

EXERCISE # J-MAIN

Q.1 Ans.(3)	Q.2 Ans.(3)	Q.3 Ans.(4)
Q.4 Ans.(1)	Q.5 Ans.(3)	Q.6 Ans.(2)
Q.7 Ans.(3)	Q.8 Ans.(4)	Q.9 Ans.(3)
Q.10 Ans.(4)	Q.11 Ans.(3)	Q.12 Ans.(3)
Q.13 Ans.(1)	Q.14 Ans.(4)	Q.15 Ans.(4)
Q.16 Ans.(4)	Q.17 Ans.(1)	Q.18 Ans.(4)
Q.19 Ans.(1)	Q.20 Ans.(1)	Q.21 Ans.(4)
Q.22 Ans.(3)	Q.23 Ans. (2)	Q.24 Ans.(3)
Q.25 Ans.(3)	Q.26 Ans.(1)	Q.27 Ans.(2)
Q.28 Ans.(1)	Q.29 Ans.(2)	Q.30 Ans.(1)
Q.31 Ans.(2)		

EXERCISE # J-ADVANCE

Q.1 Ans. pH = 11.3010	Q.2 Ans.(B)	Q.3 Ans.(A, B, C)
Q.4 Ans. $s = 1.203 \times 10^{-3} \text{M}$	Q.5 Ans. pH = 0.91325	Q.6 Ans.(A)
Q.7 Ans.(a) 0.0175% , (b) 4.757	Q.8 Ans.(C)	
Q.9 Ans.No, it will be > 7 at 0°C .	Q.10 Ans.pH = 9	Q.11 Ans.(A)
Q.12 Ans.(B)	Q.13 Ans.(D)	Q.14 Ans.(A)
Q.15 Ans.(D)	Q.16 Ans.(D)	Q.17 Ans.(8)
Q.18 Ans.(C), (D)	Q.19 Ans.(7)	Q.20 Ans.(B)
Q.21 Ans. (4.47)		

NURTURE COURSE
CHEMICAL EQUILIBRIUM

CHEMICAL EQUILIBRIUM

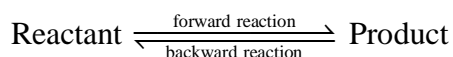
1. TYPES OF CHEMICAL REACTION :

The chemical reactions are classified on the basis of the extent to which they proceed, into the following two classes ;

I. Reversible reactions : Reaction in which entire amount of the reactants is not converted into products is termed as reversible reaction.

(i) Characteristics of reversible reactions :

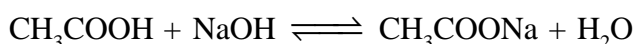
- (a) These reactions can be started from either side.
- (b) These reactions are never complete.
- (c) This sign (\rightleftharpoons) represents the reversibility of the reaction.



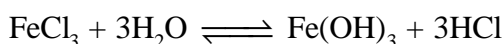
- (d) These reactions attain equilibrium and all the times, reaction mixture contains both reactant and product molecules. When reaction attains equilibrium the concentrations of reactants and product become constant (not same necessarily).

(ii) Examples of reversible reactions :

- (a) Neutralisation between an acid and a base either one or both are weak.



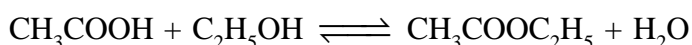
- (b) Salt hydrolysis



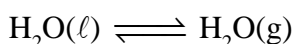
- (c) Thermal decomposition



- (d) Esterification



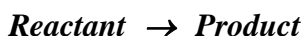
- (e) Evaporation of water in a closed vessel



II. Irreversible reactions : Reaction in which entire amount of the reactants is converted into products is termed as irreversible reaction.

(i) Characteristics of irreversible reactions :

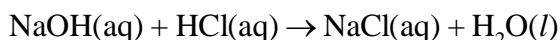
- (a) These reactions proceed only in one direction (forward direction)
- (b) These reactions can proceed to completion and reactant is completely converted into product.
- (c) The arrow (\rightarrow) is placed between reactants and products



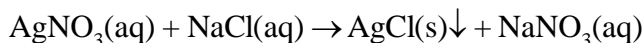
- (d) These reactions never attain equilibrium.

(ii) Examples of irreversible reactions :

- (a) Neutralisation between strong acid and strong base



- (b) Precipitation reactions

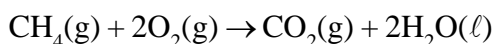


- (c) Thermal decomposition



However, if the above reaction is carried out in closed container, i.e., leaving no scope for gas to escape out, the reaction shows reversible nature.

- (d) Combustion reactions

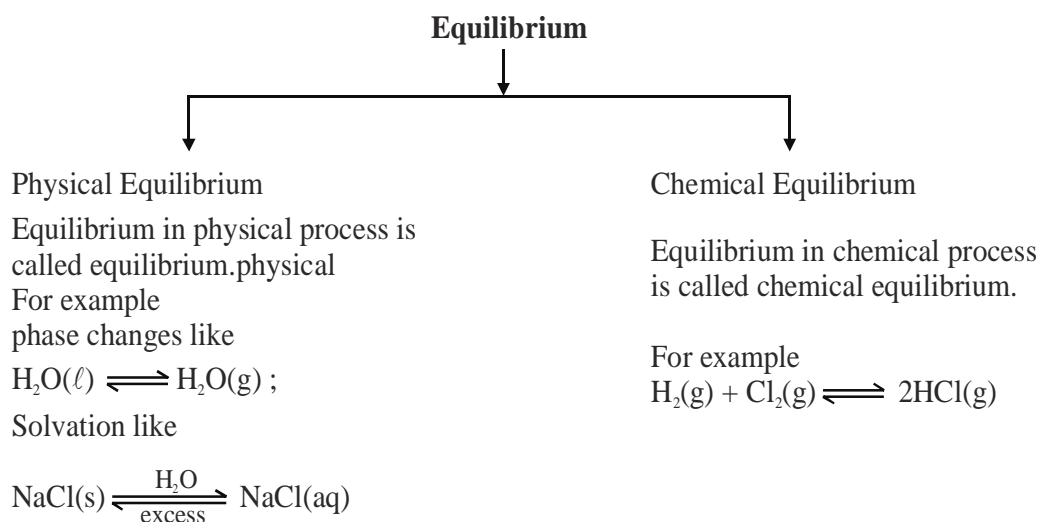


2. EQUILIBRIUM :

In the state of equilibrium, system loses its tendency for a change and all the properties associated with system like pressure, temperature, composition, etc become constant and do not vary without external stimulation. On the basis of nature of process in which state of equilibrium is attained, it may be of two types :

- (A) Physical equilibrium

- (B) Chemical equilibrium

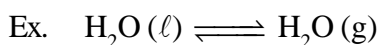


2.1 Physical equilibrium :

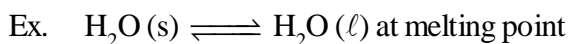
If in a system only physical state (phase) is changed and equilibrium is established, (i.e. there is no chemical change), the equilibrium is called **physical equilibrium**. Ex : Fusion of ice, evaporation of water, dissolution of salts, absorption of gases in liquid, etc.

Following are the types of common physical equilibria :

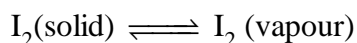
- (i) **Liquid-Vapour equilibria** : In a closed vessel, the vapours above the liquid are in equilibrium at given temperature.



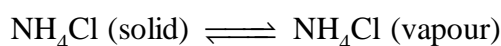
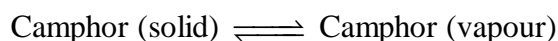
- (ii) **Solid-Liquid equilibria** : This equilibrium can be established only at melting point of solid. At this stage solid and liquid phases exist simultaneously in equilibrium.



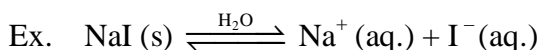
- (iii) **Solid-Vapour equilibria** : Let us now consider the systems where solids sublime to vapour phase. If we place solid iodine in a closed vessel, after sometime the vessel gets filled up with violet vapour and the intensity of colour increases with time. After certain time the intensity of colour becomes constant and at this stage equilibrium is attained. Hence solid iodine sublimes to give iodine vapour and the iodine vapour condenses to give solid iodine. The equilibrium can be represented as,



Other examples showing this kind of equilibrium are,



- (iv) **(Solute-Solvent) Saturated solution equilibria** : If the rate of dissolution of solids in liquid is equal to the rate of crystallization of solid from solution i.e. solution is saturated with respect to solid then saturated solution equilibria established, provided temperature is constant.



- (v) **(Gas + Solvent) Saturated solution equilibria** : In such equilibria, solvent is saturated with respect to gas i.e. rate of entering of gas molecules in solvent is equal to rate of escaping of gas molecules from solvents. Above phenomenon can be observed in closed container at definite temperature. Ex : Dissolved CO_2 in cold drinks, dissolved O_2 in water, etc.

Note: (i) The solubilities of gases in liquid is a function of pressure of gas over liquid.

- (ii) **Henry's law** can be applied on such system, that states, the mass of gas dissolved in a given mass of solvent at any temperature is proportional to the pressure of the gas above the solvent.

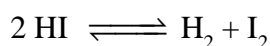
- (iii) One should not compare it with liquid vapour equilibria.

2.2 Chemical equilibrium :

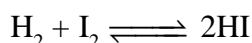
Analogous to the physical systems, chemical reactions also attain a state of equilibrium. These reactions can occur both in forward and backward directions. When the rates of the forward and reverse reactions become equal, the concentrations of the reactants and the products become constant. This is the stage of chemical equilibrium. This equilibrium consists of a forward reaction in which the reactants give product(s) and reverse reaction in which product(s) gives the original reactants.

2.2.1 Characteristics of Chemical equilibrium :

- (i) It is attained in reversible chemical reactions only.
- (ii) Equilibrium is possible only in closed system.
- (iii) In this state, all the measurable properties of the system like temperature, concentration, colour, density etc. don't undergo any change with time, i.e. constant.
- (iv) Equilibrium is dynamic in nature i.e., at microscopic level reaction is not stopped. It appears that no change is occurring but both the opposing reactions are proceeding at the same rate. So there is no net change. Thus equilibrium is not static in nature.
- (v) Chemical equilibrium can be approached from both sides



or

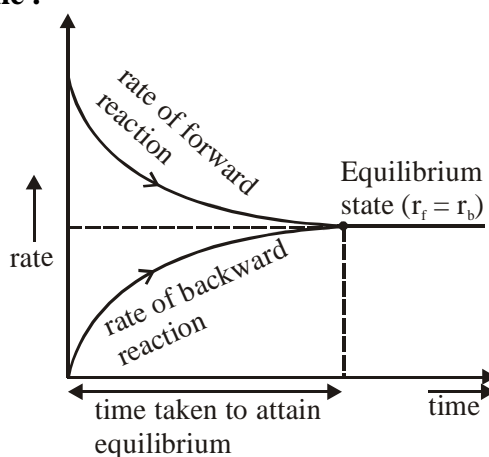


At equilibrium, reactants and products have fixed composition and this is independent of the fact whether the reaction start with the reactant or with the product.

- (vi) Equilibrium is not affected by the presence of catalyst. The catalyst only helps in attaining equilibrium rapidly.
- (vii) At equilibrium, opposing reactions (i.e., forward and backward) proceeds with equal rates.
i.e., rate of forward reaction = rate of backward reaction.

- Note:** (i) Whenever question doesn't ask about direction, then we take forward direction only.
- (ii) In a reversible reaction if forward reaction is exothermic then the backward reaction will be endothermic and vice versa.

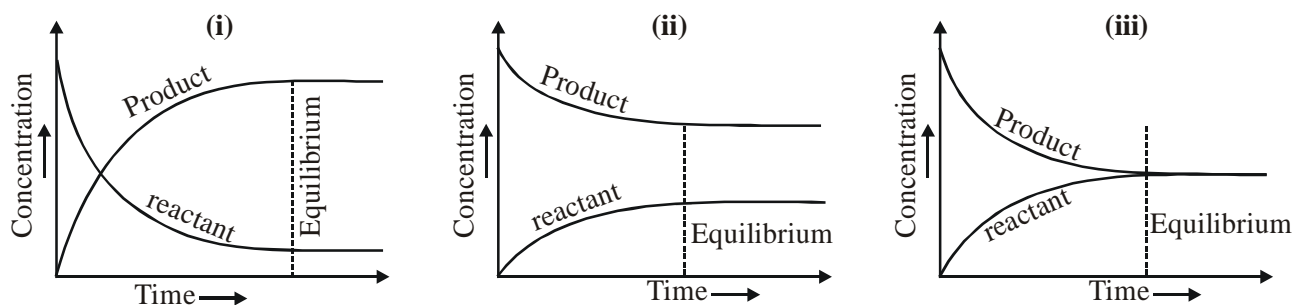
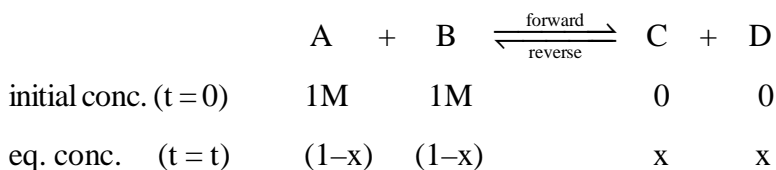
2.2.2 Variation of Rate v/s Time :



From above graph, initially rate of forward reaction decreases and the rate of backward reaction increases. At certain stage, rate of forward reaction becomes equal to rate of backward reaction called *equilibrium state*.

2.2.3 Variation of Concentration v/s Time :

Let us consider a reversible reaction,



In the beginning (at time $t = 0$), the container has only the reacting molecules A and B while the products C and D are nil. With the passage of time, the reactants A and B will be used up or consumed to form the products, C and D. It means that the concentration or molar concentration of the reactants will decrease while those of the products will increase. A stage will be ultimately reached when their concentration becomes constant i.e., there will be no further change in concentration of either of the reactants A and B or of the products C and D. This represents a state of equilibrium.

Note: At equilibrium, the concentration of reactant and product will be constant. It means, it may be different as above graph (i) & (ii) or same as above graph (iii) but the rate of forward reaction and the backward reaction will be always same.

Ex.1 Chemical equilibrium is a condition :

- (A) where all species have same concentration
- (B) where all species have constant concentration with respect to time.
- (C) where all species have unit concentration
- (D) all of above

Sol. (B)

Ex.2 Example of physical equilibria, is :

- (A) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
- (B) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
- (C) $H_2O(s) \rightleftharpoons H_2O(l)$
- (D) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

Sol. (C)

Physical equilibria does not include any chemical change.

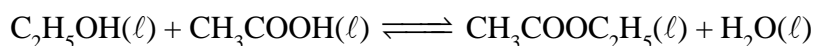
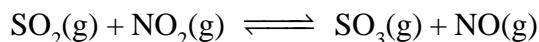
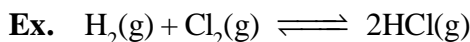
3. TYPES OF CHEMICAL EQUILIBRIUM :

I. Homogeneous equilibrium

II. Heterogeneous equilibrium

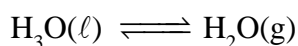
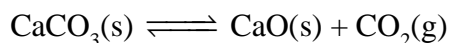
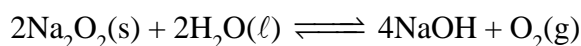
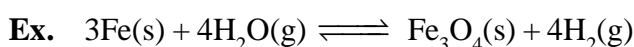
I. Homogeneous equilibrium :

It is the equilibrium when all reactants and products are in same phase.



II. Heterogeneous equilibrium :

It is the equilibrium the reactants and the products are present in different phases. All physical equilibria are heterogeneous.



4. ACTIVE MASS :

The mass of a substance which effect the rate of reaction i.e. mass of substance which take a part actively in a reaction. Active mass depends on state of substance.

(i) **Solution state :** In this state, active mass of a substance is represented by concentration (molarity).

Active mass is usually expressed in concentration by enclosing the symbol of the reactant in square bracket [].

$$\text{Active mass} = \frac{\text{moles}}{\text{Volume in litres}} = \frac{\text{grams(w)}}{\text{mol.wt.}(M_w) \times \text{Volume in litres(V)}} = \frac{w \times 1000}{M_w \times V(\text{mL})}$$

(ii) **Gaseous state :** In this state, active mass of a substance may be represented as concentration (molarity) or partial pressure.

(iii) **Pure solid & pure liquid :** In this state, active mass of solids, pure liquids and solvents in large excess is a constant quantity because there is no change in activity with the change in quantity or volume of system.

$$\text{Molar concentration (M)} = \frac{w}{M \times V} = \frac{d}{M} = \frac{\text{density of the substance}}{\text{molar mass of the substance}} = \text{constant}$$

as density of pure solids and liquids is constant and molar mass is also constant.

5. LAW OF MASS ACTION AND LAW OF EQUILIBRIUM CONSTANT :

The law of mass action is given by **Guldberg** and **Waage**. According to it, "the rate of a chemical reaction at a particular temperature is proportional to the product of active masses of reactants raised to the powers equal to their stoichiometric coefficients".

Consider a reversible reaction : $m_1A + m_2B \rightleftharpoons n_1C + n_2D$

According to law of mass action

rate of forward reaction (r_f) $\propto (a_A)^{m_1} (a_B)^{m_2}$

$$r_f = k_f(a_A)^{m_1} (a_B)^{m_2}$$

rate of backward reaction (r_b) $\propto (a_C)^{n_1} (a_D)^{n_2}$

$$r_b = k_b(a_C)^{n_1} (a_D)^{n_2}$$

At equilibrium $r_f = r_b$

$$k_f(a_A)^{m_1} (a_B)^{m_2} = k_b(a_C)^{n_1} (a_D)^{n_2}$$

$$K_{eq} = \frac{k_f}{k_b} = \frac{(a_C)^{n_1} (a_D)^{n_2}}{(a_A)^{m_1} (a_B)^{m_2}}$$

where, K_{eq} = equilibrium constant

k_f = forward rate (velocity) constant

k_b = backward rate (velocity) constant

a_A, a_B = active mass of reactant A & B

a_C, a_D = active mass of product C & D

m_1, m_2 = stoichiometry coefficient of reactant A & B

n_1, n_2 = stoichiometry coefficient of product C & D

At a given temperature, the product of molar concentrations of the reaction products raised to the respective stoichiometric coefficient in the balanced chemical equation divided by the product of molar concentrations of the reactants raised to their individual stoichiometric coefficients has a constant value. This is known as the **Equilibrium Law or Law of Chemical Equilibrium**.

5.1 Types of equilibrium constant (K_{eq}) :

(i) **Equilibrium constant in terms of concentration (K_C)** : K_C is defined for reactions in gas phase & solution phase. Molar concentrations are used to express amounts.

(ii) **Equilibrium constant in terms of partial pressure (K_P)** : K_P is defined for reactions in gas phase. Partial pressures are used to express amounts.

Ex. Consider a reversible reaction in gas phase : $m_1A + m_2B \rightleftharpoons n_1C + n_2D$

$$K_C = \frac{[C]^{n_1} [D]^{n_2}}{[A]^{m_1} [B]^{m_2}}$$

$$K_P = \frac{(P_C)^{n_1} (P_D)^{n_2}}{(P_A)^{m_1} (P_B)^{m_2}}$$

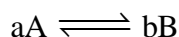
here,

$[A], [B], [C], [D]$ = Molar concentration of A, B, C, D respectively at equilibrium .

$(P_A), (P_B), (P_C), (P_D)$ = partial pressure of A, B, C, D respectively at equilibrium .

5.2 Units of equilibrium constant :

5.2.1 The value of equilibrium constant K_c can be calculated by substituting the concentration terms in mol/L or M and for K_p partial pressure is substituted in Pa, kPa, bar or atm. This results in units of equilibrium constant based on molarity or pressure, unless the exponents of both the numerator and denominator are same. For general reactions,



$$(i) \quad K_c = \frac{[B]^b}{[A]^a}$$

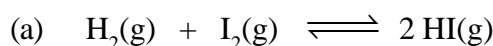
$$\text{unit of } K_c = \left(\frac{\text{mol}}{\text{L}} \right)^{b-a} = [M]^{b-a} = M^{\Delta n_g}$$

here, $\Delta n_g = b - a = \text{moles of (Product - Reactant)}$

$$(ii) \quad K_p = \frac{(P_B)^b}{(P_A)^a}$$

$$\text{unit of } K_p = (\text{atm})^{b-a} = (\text{atm})^{\Delta n_g} \text{ or } (\text{Pa})^{\Delta n_g} \text{ or } (\text{bar})^{\Delta n_g}$$

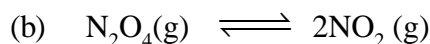
here, $\Delta n_g = b - a = \text{moles of (Product - Reactant)}$

Ex.3 Write down the expression and unit for following reaction :

$$K_c = \frac{[HI]^2}{[H_2][I_2]} \quad \left(\frac{\text{mol}}{\text{L}} \right)^0$$

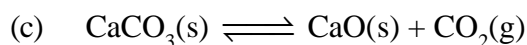
$$K_p = \frac{P_{HI}^2}{P_{H_2} P_{I_2}} \quad (\text{atm})^0$$

$\therefore K_c$ and K_p have no unit.



$$K_c = \frac{[NO_2]^2}{[N_2O_4]} \quad \left(\frac{\text{mol}}{\text{L}} \right)^1$$

$$K_p = \frac{P_{NO_2}^2}{P_{N_2O_4}} \quad (\text{atm})^1$$

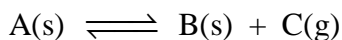


$$K_c = [CO_2] \quad \left(\frac{\text{mol}}{\text{L}} \right)^1$$

$$K_p = P_{CO_2} \quad (\text{atm})^1$$

5.2.2

Equilibrium constants is expressed in standard state that is called standard state equilibrium constant or thermodynamic equilibrium constant, which is dimensionless quantity. It is denoted by K_c^0 and K_p^0 . For a pure gas, the standard state is 1 bar. Therefore a pressure of 4 bar in standard state can be expressed as $4 \text{ bar}/1 \text{ bar} = 4$, which is a dimensionless number and concentration of 3 M solution in standard state can be expressed as $\frac{3\text{M}}{1\text{M}} = 3$, which is a dimensionless number. The numerical value of equilibrium constant depends on the standard state chosen. Thus, in this system both K_c^0 and K_p^0 are dimensionless quantities but have different numerical values due to different standard states. For example,



$$K_c = [\text{C}] \quad (\text{mol/L})$$

$$\text{but } K_c^0 \text{ is a dimensionless quantity so } K_c^0 = \frac{[\text{C}]}{1\text{M}}$$

$$K_p = P_c \quad (\text{bar})^1$$

$$\text{but } K_p^0 \text{ is a dimensionless quantity so } K_p^0 = \frac{P_c}{1 \text{ bar}}$$

5.3 Relation between K_p & K_c :

For the reaction, $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$

we can write

$$K_c = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b} \quad \dots\dots\dots(\text{i})$$

Assuming the gaseous components to behave ideally ,

$$P_i V_i = n_i RT$$

$$P_i = (n_i/V_i) RT = C_i RT = [i] RT$$

where $[i]$ is the molar concentration of the species 'i'.

$$P_A = [\text{A}]RT, P_B = [\text{B}]RT, P_C = [\text{C}]RT, P_D = [\text{D}]RT$$

$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b} = \frac{([\text{C}]RT)^c ([\text{D}]RT)^d}{([\text{A}]RT)^a ([\text{B}]RT)^b} = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b} \times (RT)^{(c+d)-(a+b)}$$

from eq..(i)

$$K_p = K_c (RT)^{(c+d)-(a+b)}$$

$$\boxed{K_p = K_c (RT)^{\Delta n_g}}$$

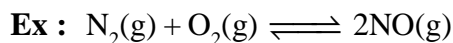
$\Delta n_g = (\text{Number of moles of gaseous products}) - (\text{Number of moles of gaseous reactants}).$

$$\Delta n_g = (c + d) - (a + b)$$

The units of K_p & K_c are not fixed and depend on stoichiometry of the reaction. In case the number of moles of the reactant & that of the product are same K_p & K_c do not have any unit.

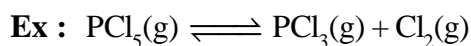
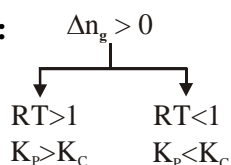
5.4 Different cases for $K_p = K_c(RT)^{\Delta n_g}$:

Case-I : If $\Delta n_g = 0$ then $K_p = K_c$



$K_p = \text{unit less} ; K_c = \text{unit less} ;$

Case-II :



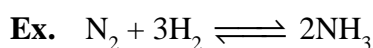
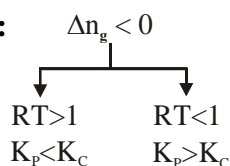
$$\Delta n_g = 2 - 1 = 1 \text{ then } K_p = K_c(RT)^1$$

if $RT > 1$ then $K_p > K_c$

if $RT < 1$ then $K_p < K_c$

Unit : $K_p = \text{atm}^1 ; K_c = \text{conc.}^1$

Case-III :



$$\Delta n_g = 2 - 4 = -2 \text{ then } K_p = K_c(RT)^{-2}$$

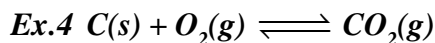
if $RT > 1$ then $K_p < K_c$

if $RT < 1$ then $K_p > K_c$

$K_p = \text{atm}^{-2} ; K_c = \text{conc.}^{-2}$

Case-IV : If $T = \frac{1}{R} = \frac{1}{0.821} \approx 12.2 \text{ K}$

$[K_p = K_c ; \text{for any value of } \Delta n_g]$



Mole of O_2 and CO_2 are 5 mole and 10 mole at equilibrium respectively, then find K_p & K_c for above reaction.

Sol. Partial pressure = Mole fraction \times Total pressure

$$P_{CO_2} = X_{CO_2} \cdot P_T = \frac{n_{CO_2}}{n_T} \times P_T = \frac{10}{15} \times P_T$$

$$P_{O_2} = X_{O_2} \cdot P_T = \frac{n_{O_2}}{n_T} \times P_T = \frac{5}{15} \times P_T$$

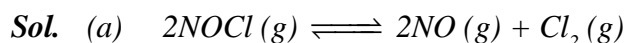
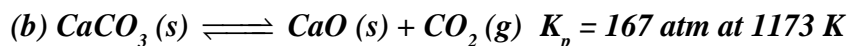
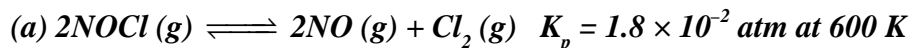
$$K_p = \frac{P_{CO_2}}{P_{O_2}}$$

$$K_p = \frac{\frac{10}{15} \times P_T}{\frac{5}{15} \times P_T} = 2$$

$$\therefore K_p = K_c (RT)^{\Delta n_g}$$

$$K_c = \frac{K_p}{(RT)^{\Delta n_g}} = \frac{2}{(RT)^0} = 2$$

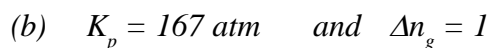
Ex.5 Find the values of K_c for each of the following equilibria from the value of K_p .



$$K_p = 1.8 \times 10^{-2} \text{ atm} \quad \text{and} \quad \Delta n_g = 3 - 2 = 1$$

$$K_p = K_c (RT)^{\Delta n_g} = K_c \times (RT)$$

$$\therefore K_c = \frac{K_p}{RT} = \frac{1.8 \times 10^{-2}}{0.0821 \times 600} = 3.65 \times 10^{-4} M$$



$$K_p = K_c (RT)^{\Delta n_g} = K_c \times (RT)$$

$$\therefore K_c = \frac{K_p}{RT} = \frac{167}{0.0821 \times 1173} = 1.734 M$$

Ex.6 In the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ the concentration of H_2 , I_2 and HI at equilibrium are 10.0, 6.0 and 28 moles per litre respectively. What will be the equilibrium constant?

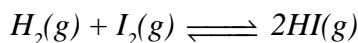
(A) 30.61

(B) 13.066

(C) 29.40

(D) 20.90

Sol.(B)



Applying law of mass action,

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

Given $[H_2] = 10 \text{ mol L}^{-1}$
 $[I_2] = 6.0 \text{ mol L}^{-1}$
 $[HI] = 28.0 \text{ mol L}^{-1}$

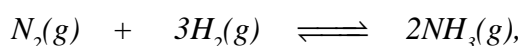
So, $K_c = \frac{(28.0)^2}{(10) \times (6.0)} = 13.066$

Ex.7 For a gas phase reaction at equilibrium,

$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$, the partial pressures of H_2 and N_2 are 0.4 and 0.8 atmosphere respectively. The total pressure of the entire system is 2.4 atmosphere. What will be the value of K_p if all the pressures are given in atmosphere ?

- (A) 32 atm^{-2} (B) 20 atm^{-2} (C) 28.125 atm^{-2} (D) 80 atm^{-2}

Sol.(C)



Partial pressures at equilibrium

$$0.8 \quad 0.4 \quad [2.4 - (0.8 + 0.4) = 1.2]$$

Applying law of mass action,

$$K_p = \frac{[P_{NH_3}]^2}{[P_{N_2}][P_{H_2}]^3} = \frac{1.2 \times 1.2}{0.8 \times 0.4 \times 0.4 \times 0.4} \Rightarrow K_p = 28.125 \text{ atm}^{-2}$$

Ex.8. $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$; Correct option for reaction is/are :

- (a) $K_p = K_c$
 (b) $K_p > K_c$
 (c) $K_p < K_c$
 (d) any of these, depending on temperature.

Sol.(D)

If (d) option is not given, then the answer is (b) because $\frac{1}{R} \approx 12.2K$ which is very low relative to room temperature.

Ex.9. For which of the following reactions, $K_p > K_c$ at $25^\circ C$ (298K)

- (a) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
 (b) $H_2(g) + I_2(s) \rightleftharpoons 2HI(g)$
 (c) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
 (d) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
 (e) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

Sol. (b, d, e)

Ex.10. For a gaseous reaction $K_p = 0.4 \text{ atm}^3$ at 27°C . Calculate K_c .

Sol. $K_p = K_c (RT)^{\Delta n}$

$$0.4 = K_c (0.0821 \times 300)^3$$

$$K_c = 2.6 \times 10^{-8} \text{ M}^3$$

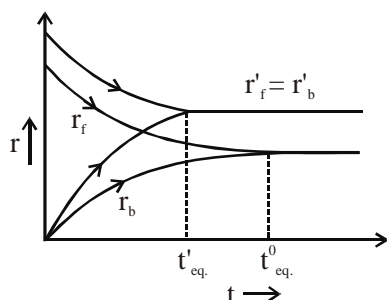
6. Characteristics of equilibrium constant :

- The expression for equilibrium constant K is applicable only when concentrations of the reactants and products have attained their equilibrium values and do not change with time.
- The value of equilibrium constant is independent of initial concentration of the reactants and product.
- Equilibrium constant has one unique value for a particular reaction represented by a balanced equation at a given temperature.
- Value of equilibrium constant is not affected by catalyst. Catalyst simply helps in attaining equilibrium earlier.

The relative increase in the rate of forward as well as backward reaction remain same on using the catalyst.

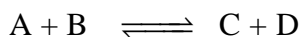
$$K_{\text{eq. uncatalyst}} = \frac{K_f}{K_b}$$

$$K_{\text{eq. catalyst}} = \frac{K_f \times x}{K_b \times x} = \frac{K_f}{K_b} = K_{\text{eq. (uncatalyst)}}$$



6.1 Factor affecting the equilibrium constant :

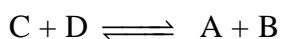
(A) Mode of representation of the reaction :



The equilibrium constant for the reaction

$$K_c = \frac{[C][D]}{[A][B]}$$

If the reaction is reversed



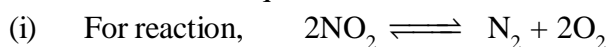
$$\text{then, } K'_c = \frac{[A][B]}{[C][D]}$$

The two equilibrium constant related as ; $K_c = \frac{1}{K'_c}$

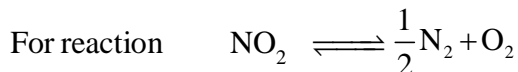
If the reaction is reversed, the value of the equilibrium constant is inverted.

(B) Stoichiometry of the reaction :

When a reversible reaction can be written with the help of two or more stoichiometric equation, the value of equilibrium constant will be numerically different.

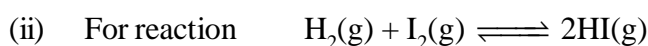


$$K_c = \frac{[\text{N}_2][\text{O}_2]^2}{[\text{NO}_2]^2}$$

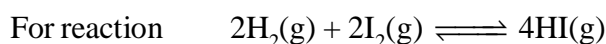


$$K'_c = \frac{[\text{N}_2]^{\frac{1}{2}}[\text{O}_2]}{[\text{NO}_2]}$$

The two constants are related as $K'_c = \sqrt{K_c}$

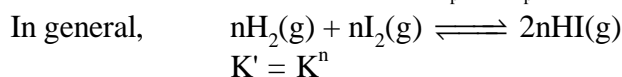


$$K_p = \frac{P_{\text{HI}}^2}{P_{\text{H}_2} \cdot P_{\text{I}_2}}$$



$$K'_p = \frac{P_{\text{HI}}^4}{P_{\text{H}_2}^2 \cdot P_{\text{I}_2}^2}$$

The two constants are related as $K'_p = K_p^2$.



When the coefficient of a balanced equation are multiplied by a common factor 'n', the equilibrium constant must be raised to the respective factor, K_{eq}^n .

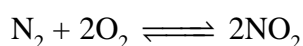
(C) Addition the reaction :



For the 1st step, $K_1 = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}$

For the 2nd step, $K_2 = \frac{[\text{NO}_2]^2}{[\text{NO}]^2[\text{O}_2]}$

from eq. (i) + (ii)



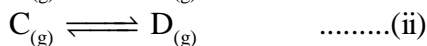
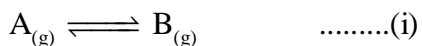
For this reaction, $K = \frac{[\text{NO}_2]^2}{[\text{N}_2][\text{O}_2]^2}$

the above reaction is related as

$$\therefore K_1 \times K_2 = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} \times \frac{[\text{NO}_2]^2}{[\text{NO}]^2[\text{O}_2]} = \frac{[\text{NO}_2]^2}{[\text{N}_2][\text{O}_2]^2} = K$$

If there is addition of two reaction then the equilibrium constant is multiplied.

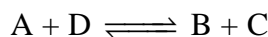
(D) Subtract the reaction :



For the (i) step, $K_1 = \frac{[B]}{[A]}$

For the (ii) step, $K_2 = \frac{[D]}{[C]}$

from eq. (i) – (ii)



For this reaction, $K = \frac{[B][C]}{[A][D]}$

the above reaction is related as, $K = \frac{K_1}{K_2} = \frac{[B]}{[A]} \times \frac{[C]}{[D]} = K$

If we subtract of two reaction, then the equilibrium constant will be divided.

Ex.11 What should be the equilibrium constant for the reaction $HI \rightleftharpoons \frac{1}{2}H_2 + \frac{1}{2}I_2$ if the equilibrium constant for the reaction $H_2 + I_2 \rightleftharpoons 2HI$ at $444^\circ C$ is 64 ?
 (A) 64 (B) 8 (C) 0.12 (D) 0.81



$$K_1 = \frac{[HI]^2}{[H_2][I_2]} \quad K_2 = \frac{[H_2]^{1/2}[I_2]^{1/2}}{[HI]}$$

Therefore, $K_2 = \frac{1}{\sqrt{K_1}} = \frac{1}{\sqrt{64}} = \frac{1}{8} = 0.12$

(E) Equilibrium constant depends upon the temperature.

The equilibrium constant of a particularly balanced reaction depends only on temperature. It is independent from all other factor like amount of components, concentration, pressure, volume etc.

$$K_{eq.} = \frac{K_f}{K_b}$$

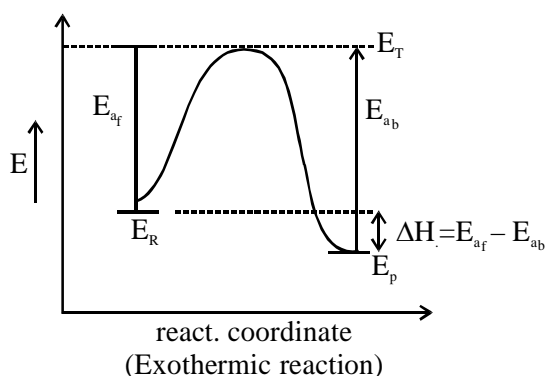
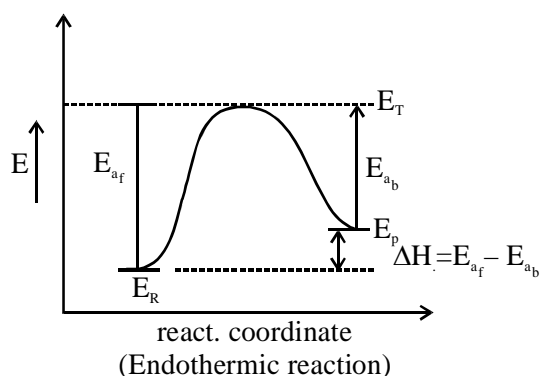
And rate constant, $K = A \cdot e^{-E_a/RT}$

Now, $K_{eq.} = \frac{K_f}{K_b} = \frac{A_f \cdot e^{-E_{af}/RT}}{A_b \cdot e^{-E_{ab}/RT}} = \frac{A_f}{A_b} \cdot e^{-(E_{af}-E_{ab})/RT}$

$$K_{eq.} = A \cdot e^{-\Delta H/RT} \quad (\text{Van't Hoff's equation})$$

where $A = \frac{A_f}{A_b} = \text{constant}$

and $\Delta H = E_{af} - E_{ab}$



If K_1 and K_2 be the equilibrium constants of a reaction at absolute temperatures T_1 and T_2 , then

$$\ln \frac{K_2}{K_1} = \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

On increasing the temperature the rate constant of reaction increases. But the reaction with higher activation energy is more sensitive towards temperature change. For the reaction of higher activation energy the value of rate constant increases largely on increasing temperature as well as the rate constant decreases largely as decrease in temperature.

For endothermic reaction

$$\begin{aligned} \Delta H &= E_{a_f} - E_{a_b} = +ve \\ \Rightarrow T \uparrow; K_{eq.} &= \frac{K_f \uparrow}{K_b \uparrow} \quad (K_f \text{ larger increasing and hence } K_{eq.} \text{ increase}) \end{aligned}$$

For exothermic reaction

$$\begin{aligned} \Delta H &= E_{a_f} - E_{a_b} = -ve \\ \Rightarrow T \uparrow; K_{eq.} &= \frac{K_f \uparrow}{K_b \uparrow} \quad (K_b \text{ larger increasing and hence } K_{eq.} \text{ decreases}) \end{aligned}$$

Ex.12 The equilibrium constant for the reaction $H_2(g) + S(s) \rightleftharpoons H_2S(g)$ is 18.5 at 925 K and 9.25 at 1000 K respectively. The enthalpy of the reaction will be :

(A) $-68000.05 \text{ J mol}^{-1}$

(B) $-71080.57 \text{ J mol}^{-1}$

(C) $-80071.75 \text{ J mol}^{-1}$

(D) $57080.75 \text{ J mol}^{-1}$

Sol.(B)

Using the relation,

$$\log \frac{K_2}{K_1} = \frac{\Delta H}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\log \frac{9.25}{18.5} = \frac{\Delta H}{2.303 \times 8.314} \times \frac{75}{925 \times 1000}$$

$$-0.301 = \frac{\Delta H \times 75}{2.303 \times 8.314 \times 925 \times 1000} \Rightarrow \Delta H = -71080.57 \text{ J mol}^{-1}.$$

Ex.13. The equilibrium $2A + B_2 \rightleftharpoons 2AB$ involves the two component equilibria,

$A + B_2 \rightleftharpoons AB + B$ and $A + B \rightleftharpoons AB$ with respective equilibrium constants K_1 and K_2 . How is the equilibrium constant, K , for the overall equilibrium related to K_1 and K_2 ?

- (A) $K = K_1 + K_2$ (B) $K = K_1 K_2$ (C) $K = K_1 / K_2$ (D) $K / 2 = K_1 K_2$

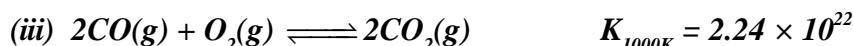
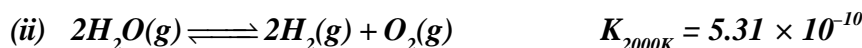
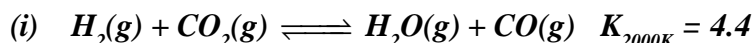
Sol. (B)

Ex.14. For the reactions :



Sol. 9.04×10^{-16}

Ex.15. From the following data :



State whether the reaction (iii) is exothermic or endothermic?

Sol. Equation (iii) = $-[2 \times (i) + (ii)]$

$$\therefore K_{2000(iii)} = \frac{1}{K_1^2 K_2} = \frac{1}{(4.4)^2 \times 5.31 \times 10^{-10}} = 9.7 \times 10^7$$

$$\therefore T \uparrow K \downarrow \Rightarrow \text{reaction is exothermic.}$$

7. APPLICATION OF EQUILIBRIUM CONSTANT :

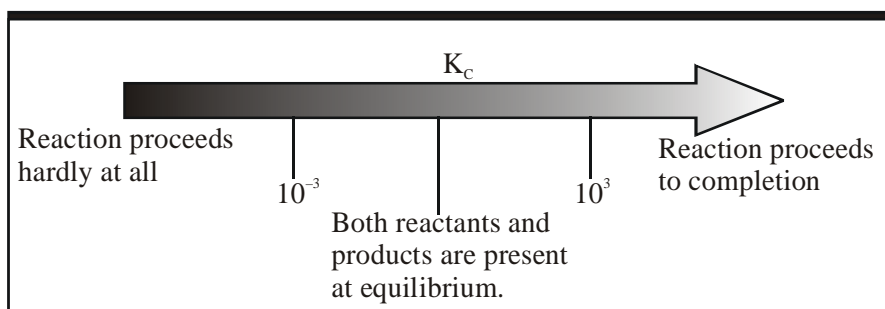
- (I) Predicting the extent of a reaction
- (II) Predicting the direction of the reaction and
- (III) Calculating equilibrium composition.

7.1 Predicting the extent of reaction :

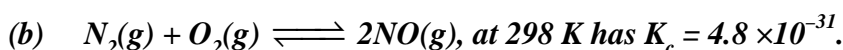
The numerical value of the equilibrium constant for a reaction indicates the extent of the reaction. But it is important to note that an equilibrium does not give any information about the rate at which the equilibrium is reached. The magnitude of K_c or K_p is directly proportional to the concentrations of products (as these appear in the numerator of equilibrium constant expression) and inversely proportional to the concentrations of the reactants (these appear in the denominator). This implies that a high value of K is suggestive of a high concentration of products and vice-versa.

We can make the following generalisations concerning the composition of equilibrium mixtures:

- (i) If $K_c > 10^3$, products predominate over reactants. If K_c is very large, the reaction proceeds almost all the way to completion.
- (ii) If $K_c < 10^{-3}$, reactants predominate over products. If K_c is very small, the reaction proceeds hardly at all.
- (iii) If K_c is in the range 10^{-3} to 10^3 , appreciable concentration of both reactants and products are present.



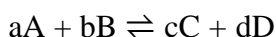
Ex.16 In the following cases which is predominant (reactant or product) for the given value of K_c .



- Sol.**
- (a) If $K_c > 10^3$, products predominate over reactants. If K_c is very large, the reaction proceeds almost all the way to completion.
 - (b) If $K_c < 10^{-3}$, reactants predominate over products. If K_c is very small, the reaction proceeds hardly at all.
 - (c) Also, gas phase decomposition of N_2O_4 to NO_2 is another reaction with a value of $K_c = 4.64 \times 10^{-3}$ at $25^\circ C$ which is neither too small nor too large. Hence, equilibrium mixtures contain appreciable concentrations of both N_2O_4 and NO_2 .

7.2 Predicting the direction of the Reaction :

The equilibrium constant is also used to find in which direction, the reaction mixture of reactants and products will proceed. For this purpose, we calculate the reaction quotient, Q . The reaction quotient is defined in the same way as the equilibrium constant (with molar concentrations to give Q_c , or with partial pressure to give Q_p) at any stage of reaction. For a general reaction:



$$Q_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Then, if $Q_c > K_c$, the reaction will proceed in the direction of reactants (reverse reaction).

if $Q_c < K_c$, the reaction will move in the direction of the products

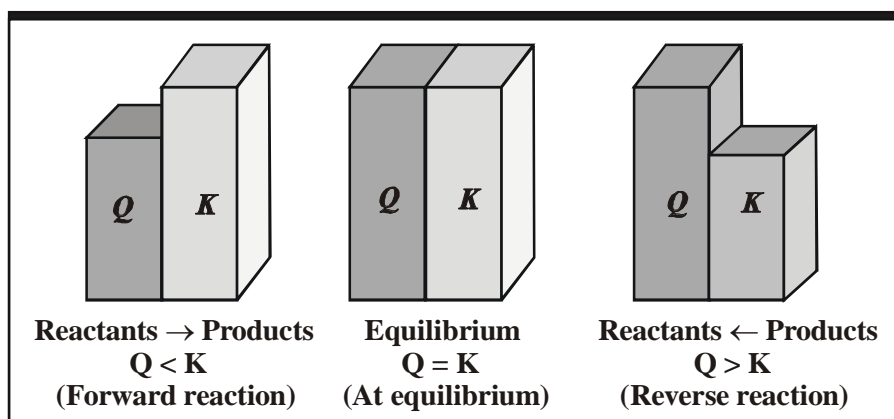
if $Q_c = K_c$, the reaction mixture is already at equilibrium.

In the reaction, $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$, if the molar concentrations of H_2 , I_2 and HI are 0.1 M, 0.2 M and 0.4 M, respectively at 783 K, then reaction quotient at this stage of the reaction is

$$Q_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(0.4)^2}{(0.1)(0.2)} = 8$$

K_c for this reaction at 783 K is 46 and we find that $Q_c < K_c$. The reaction, therefore, will move to right i.e. more $\text{H}_2(\text{g})$ and $\text{I}_2(\text{g})$ will react to form more $\text{HI}(\text{g})$ and their concentration will decrease till $Q_c = K_c$.

Thus, a reaction has a tendency to form products if $Q < K$ and to form reactants if $Q > K$.



Ex.17. For the reaction $\text{NOBr}(\text{g}) \rightleftharpoons \text{NO}(\text{g}) + \frac{1}{2} \text{Br}_2(\text{g})$

$K_p = 0.15$ atm at 90°C . If NOBr , NO and Br_2 are mixed at this temperature having partial pressures 0.5 atm, 0.4 atm and 2.0 atm respectively, will Br_2 be consumed or formed ?

Sol.
$$Q_p = \frac{[\text{P}_{\text{Br}_2}]^{1/2} [\text{P}_{\text{NO}}]}{[\text{P}_{\text{NOBr}}]} = \frac{[0.20]^{1/2} [0.4]}{[0.50]} = 0.36$$

$\therefore K_p = 0.15$

Hence, reaction will shift in backward direction

$\therefore \text{Br}_2$ will be consumed

Ex.18. Predict whether 1% CO_2 in air be sufficient to prevent any loss in weight of MgCO_3 or not.

Sol. $\text{MgCO}_3(\text{s}) \rightleftharpoons \text{MgO}(\text{s}) + \text{CO}_2(\text{g}) \quad K_p = 0.095 \text{ atm}$

$$Q = \frac{P_{\text{CO}_2}}{1} = P_{\text{CO}_2} = X_{\text{CO}_2} \cdot 1_{\text{total}}$$

$$\frac{1}{100} \times 1 \text{ atm} = 0.01 \text{ atm} < K_p$$

It will go in forward direction

0.1% CO_2 is not sufficient

Ex.19. Predict whether $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s})$ be efflorescent or $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}(\text{s})$ be hygroscopic and vapour pressure of H_2O at $25^\circ\text{C} = 0.04 \text{ atm}$.

Sol. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{CuSO}_4 \cdot 3\text{H}_2\text{O}(\text{s}) + 2\text{H}_2\text{O}(\text{g})$ $K_p = 4 \times 10^{-4} \text{ atm}$

Partial pressure of H_2O at eq. = $P_{\text{H}_2\text{O}}$

$$K_p = P_{\text{H}_2\text{O}}^2$$

$$P_{\text{H}_2\text{O}} = \sqrt{4 \times 10^{-4}} = 2 \times 10^{-2} \text{ atm}$$

$$Q = 4 \times 10^{-2} \text{ atm}$$

So, $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ be hygroscopic in this condition.

Ex.20. In above problem what maximum humidity for which $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s})$ work as efflorescent.

Sol. $\left(0.04 \times \frac{x}{100}\right)^2 < 4 \times 10^{-4}$

$$0.16 \times 10^{-4} \times \frac{x^2}{10000} < 4 \times 10^{-4}$$

$$x^2 < 50$$

$$x < 50\%$$

Max. R.H. = 50% Ans.

Ex.21. Study the following reaction



(i) Which of the following is best dehydrating drying agent.

- | | |
|--|----------|
| (A) A. $2\text{H}_2\text{O}(\text{g})$ | (D) A(s) |
| (B) B. $3\text{H}_2\text{O}(\text{g})$ | (E) B(s) |
| (C) C. $4\text{H}_2\text{O}(\text{g})$ | (F) C(s) |

$$A \rightarrow K_p = P_{\text{H}_2\text{O}}^2 \Rightarrow P_{\text{H}_2\text{O}} = 0.02 \text{ atm}$$

$$B \rightarrow K_p = P_{\text{H}_2\text{O}}^3 \Rightarrow P_{\text{H}_2\text{O}} = 0.03 \text{ atm}$$

$$C \rightarrow K_p = P_{\text{H}_2\text{O}}^4 \Rightarrow P_{\text{H}_2\text{O}} = 0.04 \text{ atm}$$

For the best dehydrating agent the moisture remained must be minimum.

(ii) If A(s), B(s) and C(s) are placed in a room where $P_{\text{H}_2\text{O}}(\text{g}) = 0.025 \text{ atm}$, which will act as dehydrating agent.

- | | | | |
|----------|-----------------|----------|---------|
| (A) A(s) | (B) B(s) & C(s) | (C) B(s) | (D) All |
|----------|-----------------|----------|---------|

(iii) Which of the following will be efflorescent at 7.5% R.H. if aqueous terim = 0.04 atm.

- | | |
|--|--|
| (a) Only A. $2\text{H}_2\text{O}(\text{s})$ | (b) Only B. $3\text{H}_2\text{O}(\text{s})$ |
| (c) Only C. $4\text{H}_2\text{O}(\text{s})$ | (d) Only A. $2\text{H}_2\text{O}(\text{s})$ & B. $3\text{H}_2\text{O}(\text{s})$ |
| (e) Only B. $3\text{H}_2\text{O}(\text{s})$ & C. $4\text{H}_2\text{O}(\text{s})$ | |

Sol. (i) D (ii) A (iii) C

7.3

Calculating equilibrium concentrations :

In case of a problem in which we know the initial concentrations but do not know any of the equilibrium concentrations, the following three steps shall be followed :

Step 1. Write the balanced equation for the reaction.

Step 2. Under the balanced equation, make a table that lists for each substance involved in the reaction :

- (a) the initial concentration,
- (b) the change in concentration on going to equilibrium, and
- (c) the equilibrium concentration.

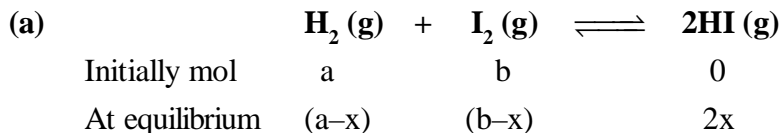
In constructing the table, define x as the concentration (mol/L) of one of the substances that reacts on going to equilibrium, then use the stoichiometry of the reaction to determine the concentrations of the other substances in terms of x .

Step 3. Substitute the equilibrium concentrations into the equilibrium equation for the reaction and solve for x . If you are to solve a quadratic equation choose the mathematical solution that makes chemical sense.

Step 4. Calculate the equilibrium concentrations from the calculated value of x .

Step 5. Check your results by substituting them into the equilibrium equation.

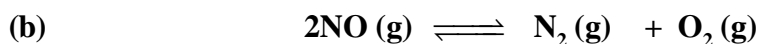
7.3.1 Some General Equilibrium Expressions :



$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-x}{V}\right)} = \frac{4x^2}{(a-x)(b-x)}$$

$$K_p = \frac{(p_{\text{HI}})^2}{p_{\text{H}_2} \times p_{\text{I}_2}} = \frac{\frac{(2x)^2}{(a+b)^2} P^2}{\left(\frac{a-x}{a+b} \cdot P\right)\left(\frac{b-x}{a+b} \cdot P\right)} = \frac{4x^2}{(a-x)(b-x)}$$

So $K_c = K_p$ ($\Delta n_g = 0$)



Initially mol	a	0	0
At equilibrium	(a-x)	x/2	x/2

$$K_c = \frac{[\text{N}_2][\text{O}_2]}{[\text{NO}]^2} = \frac{x/2 \times x/2}{(a-x)^2} = \frac{x^2}{4(a-x)^2} = K_p \quad (\Delta n_g = 0)$$



Initially mol	a	b	0	0
At equilibrium	(a-x)	(b-x)	x	x

$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]} = \frac{x^2}{(a-x)(b-x)}$$

K_p should not be given for this reaction ,



Initially mol	a	0	0
At equilibrium	(a-x)	x	x
Active mass	$\frac{(a-x)}{v}$	$\frac{x}{v}$	$\frac{x}{v}$

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{\frac{x}{v} \times \frac{x}{v}}{\frac{(a-x)}{v}} = \frac{x^2}{(a-x)v}$$

$$K_p = \frac{p_{\text{PCl}_3} \times p_{\text{Cl}_2}}{p_{\text{PCl}_5}} = \frac{\left(\frac{x}{a+x} \cdot P\right) \times \left(\frac{x}{a+x} \cdot P\right)}{\left(\frac{a-x}{a+x}\right) P} = \frac{x^2 P}{(a+x)(a-x)} = \frac{x^2 P}{a^2 - x^2}$$

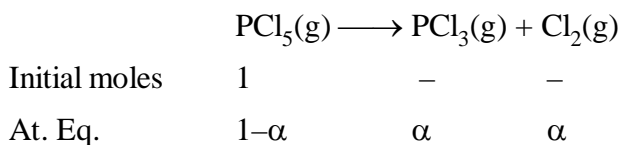


Initially mol	a	b	0
At equilibrium	(a-x)	(b-3x)	2x
Active mass	$\frac{(a-x)}{v}$	$\left(\frac{b-3x}{v}\right)$	$\left(\frac{2x}{v}\right)$

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{\left(\frac{2x}{v}\right)^2}{\left(\frac{a-x}{v}\right)\left(\frac{b-3x}{v}\right)^3} = \frac{4x^2 v^2}{(a-x)(b-3x)^3}$$

$$K_p = \frac{(p_{\text{NH}_3})^2}{p_{\text{N}_2} \times (p_{\text{H}_2})^3} = \frac{\left[\frac{2xP}{a+b-2x}\right]^2}{\left[\frac{(a-x)P}{(a+b-2x)}\right]\left[\frac{(b-3x)P}{(a+b-2x)}\right]^3} = \frac{4x^2(a+b-2x)^2}{(a-x)(b-3x)^3 P^2}$$

(g) Equilibrium constant expressions in term of ' α '



$$K_C = \frac{\alpha^2}{1-\alpha} \left(\frac{1}{V} \right) \quad \text{and} \quad K_P = \frac{\alpha^2}{1-\alpha^2} P_T$$

(h) Degree of dissociation in terms of molar mass and vapour density

(i) $\text{A}(\text{g}) \rightleftharpoons n\text{B}(\text{g})$

$$\alpha = \frac{M_T - M_O}{M_O(n-1)} \quad \text{or} \quad \alpha = \frac{D_T - D_O}{D_O(n-1)}$$

M_T = Theoretical molar mass of reactant

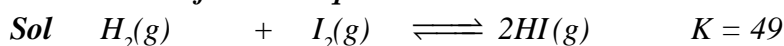
M_O = Observed molar mass of mixture

$$D_T = \frac{M_T}{2} \quad \text{and} \quad D_O = \frac{M_O}{2}$$

(ii) $n\text{A}(\text{g}) \rightleftharpoons \text{A}_n(\text{g})$

$$\alpha = \frac{M_T - M_O}{M_O \left(\frac{1}{n} - 1 \right)}$$

Ex.22 5 moles H_2 gas and 5 moles iodine-vapours are taken in vessel of 10 L capacity. Determine the moles of each at equilibrium.



$$49 = \frac{(2x)^2 v^2}{(5-x)(5-x)v^2}$$

$$49 = \frac{(2x)^2}{(5-x)^2}$$

$$7 = \frac{2x}{5-x}$$

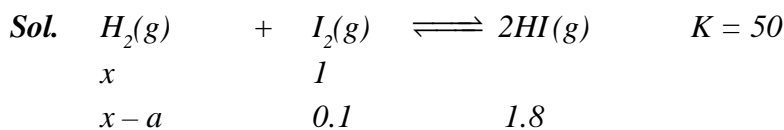
$$35 - 7x = 2x$$

$$35 = 9x$$

$$x = \frac{35}{9}$$

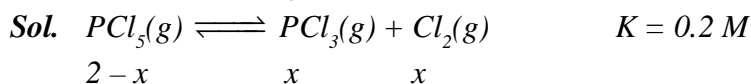
$$\text{Moles at equilibrium} = \frac{10}{9}, \frac{10}{9}, \frac{70}{9}$$

Ex.23 How many moles of $H_2(g)$ should be mixed with each mole I_2 vapours in order to convert 90% of it into HI .



$$50 = \frac{3.24}{(x-0.9)(0.1)} \Rightarrow x = 1.548$$

Ex.24 2 moles of $PCl_5(g)$ is taken in 10 l vessel. Calculate its concentration at equilibrium.



$$\frac{2-x}{v} \quad \frac{x}{v} \quad \frac{x}{v}$$

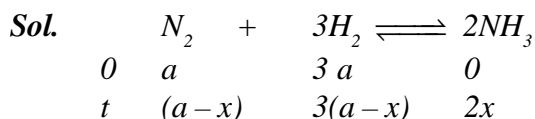
$$0.2 = \frac{\left(\frac{x}{v}\right)^2}{\left(\frac{2-x}{v}\right)} \Rightarrow x = 1.24$$

$$[PCl_5] = 0.076 M$$

$$[PCl_3] = 0.124 M$$

$$[Cl_2] = 0.124 M$$

Ex.25 1 : 3 molar ratio mixture of N_2 and H_2 yields 20% by mole NH_3 at 30 atm; calculate K_p for the equilibrium represented by



$$\text{Total moles} = 4a - 2x$$

$$X_{NH_3} = 0.2 = \frac{2x}{4a-2x} \Rightarrow 2x = 0.8a - 0.4x \Rightarrow x = a/3$$

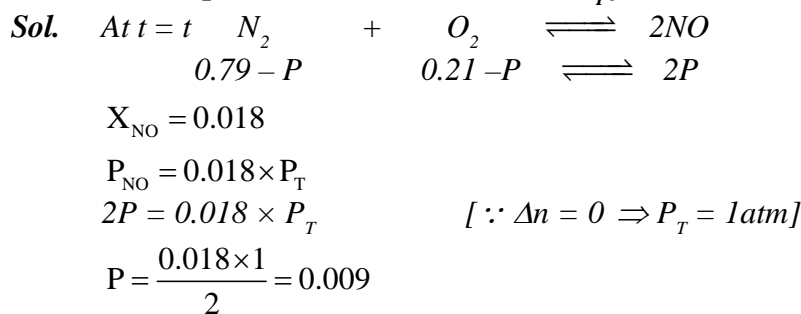
$$P_{NH_3} = 0.2 \times 30 = 6 \text{ atm}$$

$$P_{NH_3} = X_{N_2} \times P_T = \frac{a-x}{4a-2x} \times 30 = 0.2 \times 30 = 6 \text{ atm}$$

$$P_{H_2} = \frac{3(a-x)}{4a-2x} = 0.6 \times 30 = 18 \text{ atm}$$

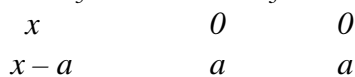
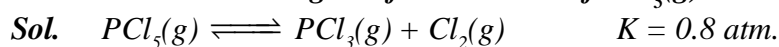
$$\therefore K_p = \frac{[P_{NH_3}]^2}{[P_{N_2}][P_{H_2}]^3} = \frac{6}{6 \times (18)^2} = 1.03 \times 10^{-3} \text{ atm}^{-2}$$

Ex.27 An air sample containing 21:79 (mole ratio) of O_2 & N_2 is heated to $2400^\circ C$. If the mole percent of NO at equilibrium is 1.8%, calculate K_p for the reaction $N_2 + O_2 \rightleftharpoons 2NO$.



$$K_p = \frac{[P_{NO}]^2}{P_{N_2} \times P_{O_2}} = \frac{(0.018)^2}{(0.781)(0.201)} = 2.06 \times 10^{-3}$$

Ex.28 Calculate the degree of dissociation of $PCl_5(g)$ at 20 atm.



Total mole = $x + a$

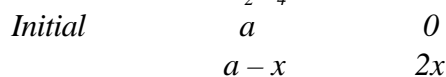
$$\frac{x-a}{x+a}(20) \quad \frac{a}{x+a}20 \quad \frac{a}{x+a}20$$

$$0.8 = \frac{\left(\frac{a}{x+a}\right)^2 (20)^2}{\left(\frac{x-a}{x+a}\right) 20} \Rightarrow 0.04 = \frac{a^2}{x^2 - a^2}$$

$$\frac{x}{a} = \frac{1}{\sqrt{26}} = 0.2$$

$$\alpha = 0.2$$

Ex.28 The vapour density a sample of $N_2O_4(g)$ is 40 at 10 atm. Calculate K_p for the reaction.



Total mole = $(a - x) + 2x = a + x$

$$\frac{a-x}{a+x}P \quad \frac{2x}{a+x}P$$

$$V.D. = \frac{M_{avg}}{2}$$

$$M_{avg} = 2 \times 40 = 80$$

$$M_{avg} = \frac{\text{Total mass}}{\text{Total moles}} = \frac{92a}{a+x} = 80$$

$$x = \frac{12}{80}a = 0.15a$$

$$K_p = \frac{4x^2}{a^2 - x^2} = 9.2 \times 10^{-2}$$

Ex.29 At what pressure an equimolar mixture of $\text{PCl}_5(\text{g})$ and $\text{Cl}_2(\text{g})$ should be taken in order to convert 75% of PCl_5 into PCl_3 .

Sol. $\text{PCl}_5(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) \quad K_p = 0.4 \text{ atm}$

Initial	a	0	
Final	$a - 0.75a$ $= 0.25a$	$a - 0.75a$ $= 0.25a$	$0.75a$

Total mole = $1.25a$

Equ. par. pr.	$\frac{0.25a \times P}{1.25a}$	$\frac{0.25a \times P}{1.25a}$	$\frac{0.75a \times P}{1.25}$
	$\frac{P}{5}$	$\frac{P}{5}$	$\frac{3P}{5}$

$$K_p = \frac{P_{\text{PCl}_3}}{P_{\text{PCl}_5} P_{\text{Cl}_2}} \Rightarrow 0.4 = \frac{\frac{3P}{5}}{\frac{P}{5} \times \frac{P}{5}} \Rightarrow P = 37.5$$

But this is pressure at equilibrium but we have to find initial pressure

Now, from $PV = nRT$

$$\frac{P_1}{P_2} = \frac{n_1}{n_2} \Rightarrow \frac{P_1}{37.5} = \frac{2}{1.25} \Rightarrow P = 60 \text{ atm}$$

Alternate method :

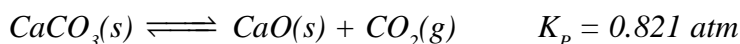
	$\text{PCl}_5(\text{g})$	+	$\text{Cl}_2(\text{g})$	\rightleftharpoons	$\text{PCl}_3(\text{g})$
Initial partial pressure	P_0		P_0		0
E.P.P.	$P_0 - 0.75P_0$ $= 0.25P_0$		$P_0 - 0.75P_0$ $= 0.25P_0$		$0.75P_0$

$$0.4 = \frac{0.75P_0}{0.25P_0 \times 0.25P_0} \Rightarrow P_0 = 30 \text{ atm}$$

\therefore Initial total pressure of mixture = $P_0 + P_0 = 60 \text{ atm}$

Note : In any problem related with relative extent of reaction, initial mole may be taken as 1 but the initial pressure or concentration should not be taken as 1.

Ex.30 100 gm CaCO_3 is taken in 30 l empty vessel and the vessel is sealed and the sample is heated to 627°C . Calculate the mass % of CaCO_3 decomposed.



Sol. $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$

Initial	1 mole	0	0
Final	$1 - x$	x	x

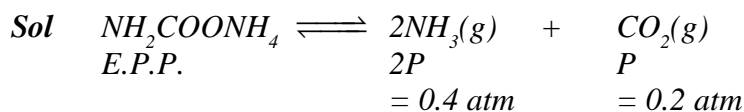
Total mole = $1 + x$

$$K_p = \frac{P_{\text{CO}_2}}{1} = P_{\text{CO}_2} \Rightarrow P_{\text{CO}_2} = \frac{nRT}{V}$$

$$0.821 = \frac{x \times 0.0821 \times 900}{30} \Rightarrow x = \frac{1}{3}$$

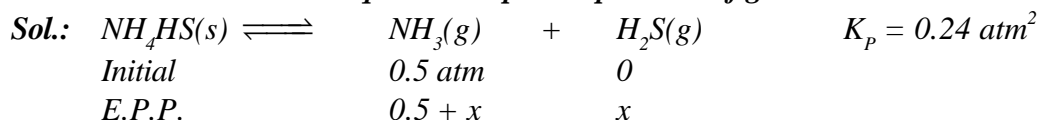
$$\% \text{ of } \text{CaCO}_3 \text{ decomposed} = \frac{1}{3} \times 100 = \frac{100}{3} \%$$

Ex.31 Some solid ammonium carbamate $\text{NH}_4\text{COONH}_4$ is taken in a evacuated vessel and the vessel is sealed after a very long time a constant pressure of 0.6 atm is observed due to dissociation of the solid into NH_3 and CO_2 gas. Calculate the dissociation constant of solid.



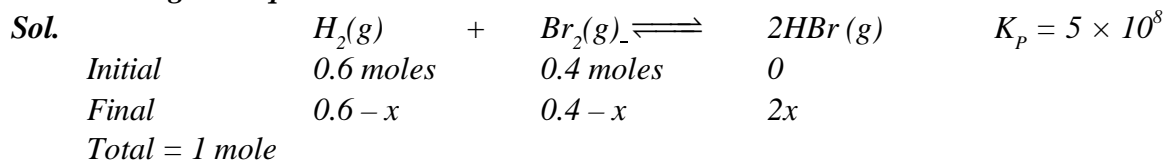
$$K_p = \frac{[0.4]^2 [0.2]}{1} = 0.032 \text{ atm}^3$$

Ex.32 Some solid ammonium hydrogen sulphide NH_4HS is in a vessel containing ammonium gas at 0.5 atm. Calculate the equilibrium partial pressure of gas.



$$K_p = \frac{P_{\text{NH}_3}}{1} \cdot P_{\text{H}_2\text{S}} \Rightarrow 0.24 = (0.5 + x)x \Rightarrow x = 0.3 \text{ atm.}$$

Ex.33 0.6 moles of $\text{H}_2(\text{g})$ and 0.4 moles of Br_2 vapour are allowed to react. Calculate the moles of each gas at equilibrium.



$$K = \frac{(2x)^2}{(0.6-x)(0.4-x)} = \frac{4x^2}{x^2 - x + 0.24}$$

$$(5 \times 10^8 - 4)x^2 - 5 \times 10^8 x + 1.2 \times 10^8 = 0$$

$$5 \times 10^8 x^2 - 5 \times 10^8 x + 1.2 \times 10^8 = 0$$

$$8x^2 - x + 0.24 = 0$$

$$x = 0.4, 0.6 (\text{Not acceptable})$$

As K_p is much larger than 1000 the reaction almost completes.

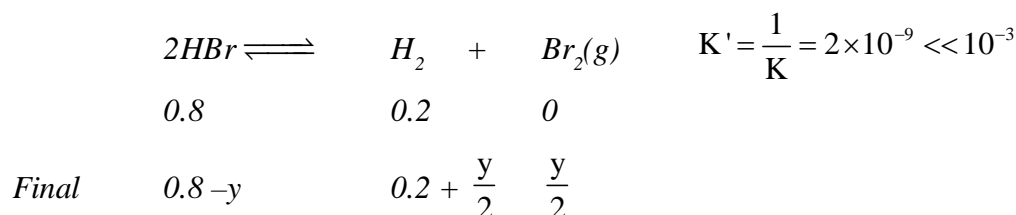
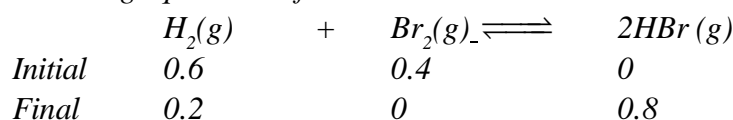
$$\text{Final moles of HBr} = 0.8$$

$$\text{Final moles of H}_2 = 0.2$$

But Final moles of $\text{Br}_2 \neq 0$

Note :

The final moles of Br_2 may be calculated by first completing the reaction in forwards direction and then achieving equilibrium from backward direction.



$$K' = \frac{[H_2][Br_2]}{[HBr]^2} = 2 \times 10^{-9} = \frac{\left(0.2 + \frac{y}{2}\right) \frac{y}{2}}{(0.8 - y)^2}$$

As K' is very small we may assume that $0.8 - y \simeq 0.8$

and, $0.2 + \frac{y}{2} \simeq 0.2$

$$\therefore 2 \times 10^{-9} = \frac{0.2 \times \frac{y}{2}}{0.64}$$

$$y = 1.28 \times 10^{-8}$$

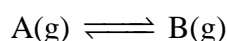
Final moles $HBr = 0.8 - y \simeq 0.8$

$$H_2 = 0.2 + \frac{y}{2} \simeq 0.2$$

$$Br_2 = \frac{y}{2} = 6.4 \times 10^{-9}$$

Ex.34 Calculate concentration of A at equilibrium for a reaction, $A(g) \rightleftharpoons B(g)$; $K_C = 10^{50}$, if the initial concentration of A is 2 M.

Sol.



initial conc.	2	0
Change in conc.	- x	x
equib. conc.	2-x	0+x

K_C is very-very high so maximum reactant converted into product.

$$\therefore \frac{K_C}{\text{initial conc.}} \geq 10^3 \text{ then } \frac{10^{50}}{2} \geq 10^3.$$

So $2-x \simeq 0 \Rightarrow x \simeq 2$ but reactant never zero.

equib. conc. $2-x \simeq y$ $x \simeq 2$

$$K_C = \frac{[B]}{[A]}$$

$$10^{50} = \frac{x}{2-x}$$

$$10^{50} = \frac{2}{y} \Rightarrow y = 2 \times 10^{-50} \text{ M}$$

$$[A] = 2 \times 10^{-50} \text{ M}$$

8. LE CHATELIER'S PRINCIPLE :

Le Chatelier's principle is applicable for any system in equilibrium which states as :

When a system in equilibrium is disturbed by external agency, the system tends to attain again an equilibrium by adjusting itself. These are these some factors by which a system in equilibrium can be disturbed.

- (i) Changing the concentration of reactant and product.
- (ii) Changing the pressure (or volume) of the system.
- (iii) Changing the temperature.

For a chemical reaction in equilibrium, Le Chatelier's principle can be stated as,

If we change concentration, pressure or temperature of a chemical reaction in equilibrium, the equilibrium will shift to the right or the left so as to minimise the change.

8.1 Effect of a change in concentration :

- (a) If more reactant is added or some product is removed from an equilibrium mixture having equilibrium constant K then the reaction moves in the forward direction (as $Q_c < K_c$) to give a new equilibrium and more products are produced.
- (b) If more product are added to or some reactant are removed from an equilibrium mixture, the reaction moves in the reverse direction (as $Q_c > K_c$) to give a new equilibrium and more reactant are produced.

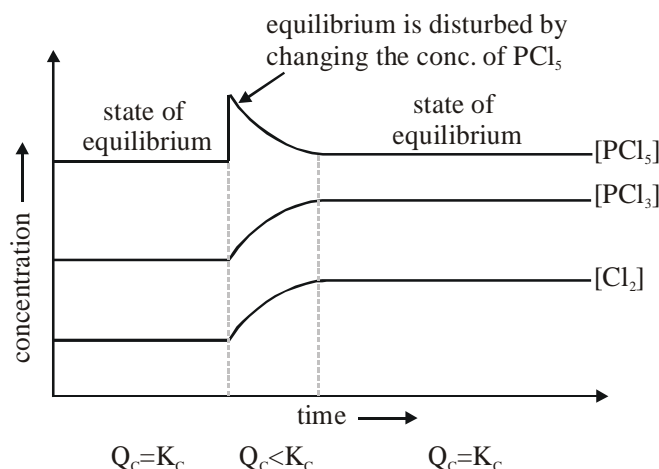
Ex. The decomposition of gaseous PCl_5 is a reversible reaction, $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$. Let the equilibrium concentrations of PCl_5 , PCl_3 and Cl_2 are respectively $[\text{PCl}_5]$, $[\text{PCl}_3]$ and $[\text{Cl}_2]$. The K_c for this reaction can be written as :

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} \text{ Also we know that at equilibrium } K_c = Q_c.$$

Case-I : Let the concentration of PCl_5 is doubled to disturb the equilibrium. This will change the reaction quotient, Q_c to :

$$Q_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[2\text{PCl}_5]} = \frac{1}{2} \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{K_c}{2}$$

After disturbing the equilibrium, the value of Q_c becomes less than K_c . In order to restore the Q_c value to K_c , the concentration of PCl_5 must be decreased while the concentrations of PCl_3 and Cl_2 are to be increased. This is achieved by favoring the forward reaction.

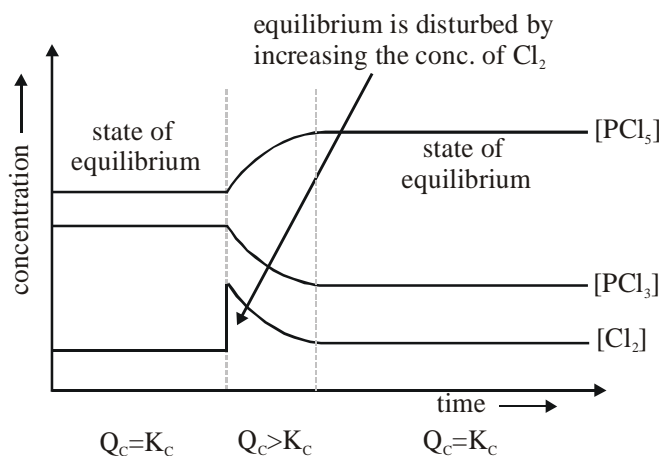


The forward reaction is also favored by removing the products from the reaction mixture (decrease in the concentration of products). Upon removal of products, the rate of forward reaction becomes greater than that of backward reaction momentarily. This will also decrease the reaction quotient. Hence the system tries to reestablish the equilibrium by converting more reactants to products so as to make the rates of both forward and backward reactions become equal again.

Case-II : For example, in case of the decomposition of PCl_5 , if the concentration of Cl_2 is increased by two times at equilibrium, the Q_c value becomes greater than the K_c value.

$$Q_c = \frac{[PCl_3][2Cl_2]}{[PCl_5]} = 2 \times \frac{[PCl_3][Cl_2]}{[PCl_5]} = 2K_c$$

Hence the system tries to restore the value of Q_c to K_c again. The backward reaction is favored to decrease the concentration of Cl_2 . However the concentration of PCl_3 also decreases automatically while the concentration of PCl_5 increases while doing so.



8.2 Effect of a change in pressure :

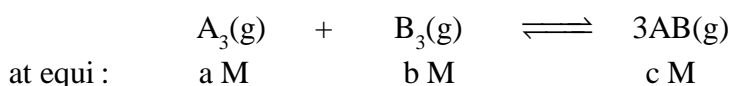
We know that, if we increase the volume of container then the pressure of the container decreases and if we decrease the volume of container then the pressure of the container increases.

$$\text{i.e., Pressure (P)} \propto \frac{1}{\text{Volume (V)}}$$

Hence, if the pressure is decreased by increasing the volume of a reaction mixture, the reaction shifts in the direction of more moles of gas while if the pressure is increased by decreasing the volume of a reaction mixture, the reaction shifts in the direction of fewer moles of gas.

Here moles of reactant or product means co-efficients of reactant or product.

(a) Suppose a general equation



For this reaction, moles of product > moles of reactant i.e., $[\Delta n = (3 - 2) > 0]$

$$K_c = \frac{(c)^3}{a \times b}$$

If we increase the pressure of the system from 0.5 atm pressure to 1 atm pressure by decreasing the volume of container from 5 litre to 2.5 litre. Hence, concentration of all the reactant and product will change and it will be greater than the initial value. Hence we can say that,

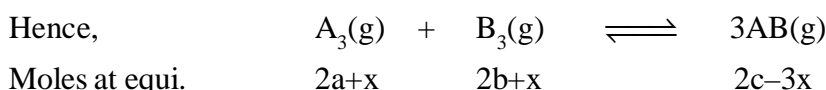
If pressure becomes double then volume becomes half and hence concentration becomes double as

$$(\text{Concentration} \propto \frac{\text{Moles}}{\text{Volume}})$$

\therefore Concentration \propto Pressure

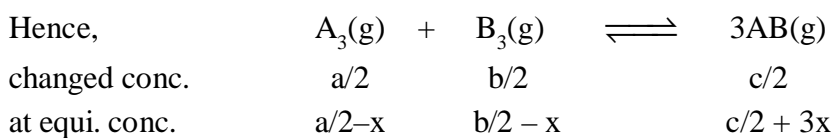
$$Q_c = 2 \times \frac{c^3}{a \times b} > K_c$$

Hence reaction will move from right to left i.e., in the backward direction.



It can be simply said that, reaction will move from right to left by increasing the pressure of the system as moles of product > moles of reactant i.e., move in the direction of fewer moles.

(b) If pressure decreases from 1 atm to 0.5 atm. Volume will increase by factor 2 concentration will decrease by factor 1/2



$$Q_c = \frac{(c/2)^3}{a/2 \times b/2} = \frac{1}{2} \frac{c^3}{a \times b} < K_c$$

$$\text{i.e., } Q_c < K_c$$

Therefore, reaction will move from left to right and as moles of product > moles of reactants, therefore reaction will move from left to right by decreasing the pressure of the system i.e. move in the direction of greater moles.

- (c) If moles of reactant = moles of product i.e., $\Delta n = 0$ then change in pressure of equilibrium mixture has no effect i.e. at this position $Q_c = K_c$ will always exist.

8.3 Effect of a change in temperature :

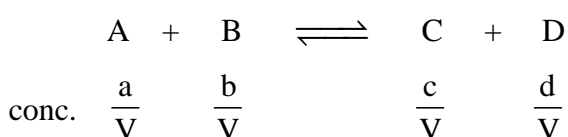
On increasing the temperature equilibrium shifts in the direction of absorption of heat (endothermic direction)

8.4 EFFECT OF INERT GAS AT THE EQUILIBRIUM :

(i) Effect of inert gas at constant volume :

When the addition of inert gas (non-reacting gas) is carried out at constant volume (V), the equilibrium remains unaffected for reactions whether they have $\Delta n = 0$ or $\Delta n \neq 0$.

Let us consider a general equation at temperature T K, and a, b, c and d are the moles of A, B, C and D respectively,



Since, V = constant, so addition of inert gas has no effect on equilibrium

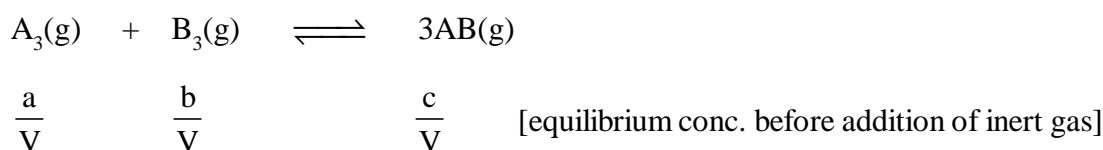
$\therefore \frac{a}{V}, \frac{b}{V}, \frac{c}{V}$ and $\frac{d}{V}$ will not change

$$Q_c = K_c \quad \text{or} \quad Q_p = K_p$$

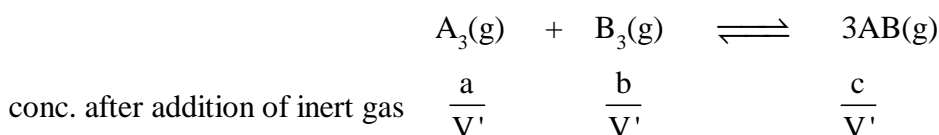
(ii) Effect of inert gas at constant pressure :

- (a) The addition of an inert gas at constant pressure to an equilibrium, the equilibrium shifts in the direction of greater number of moles.

At constant pressure, addition of inert gas or non-reacting gas means increase in volume of the system. Suppose a reaction having $\Delta n > 0$ and a, b, c and d are the moles of A, B, C and D respectively and V be the volume before addition of inert gas.



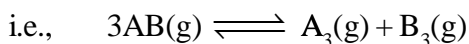
Let us consider V' be the total volume of the system after addition of inert gas So, $V' > V$



$\therefore \frac{a}{V'} < \frac{a}{V}, \frac{b}{V'} < \frac{b}{V}$ and $\frac{c}{V'} < \frac{c}{V}$

$$\text{Now, } K_c = \frac{\left(\frac{c}{V}\right)^3}{\left(\frac{a}{V}\right)\left(\frac{b}{V}\right)} = \frac{1}{V} \times \frac{c^3}{a \times b} \quad \text{and} \quad Q_c = \frac{\left(\frac{c}{V'}\right)^3}{\left(\frac{a}{V'}\right)\left(\frac{b}{V'}\right)} = \frac{1}{V'} \times \frac{c^3}{a \times b}$$

$K_c > Q_c$, hence reaction will move from left to right (forward direction) as $\Delta n > 0$ and similarly we can prove that for a reaction having $\Delta n < 0$

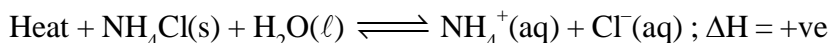


For this reaction $K_c < Q_c$, after addition of inert gas. Hence, reaction will move from right to left (reverse direction) as $\Delta n < 0$.

8.5 APPLICATION OF LE-CHATELIER'S PRINCIPLE :

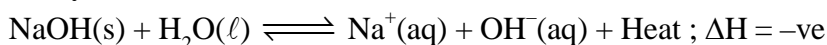
The principle is applicable not only to chemical equilibria but also to physical equilibria in similar way.

- (a) Dissolution of ammonium chloride in water



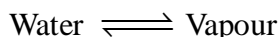
With rise in temperature, equilibrium will shift in direction which will lower the temperature counteract the effect. So, equilibrium shifts in forward direction which is endotherm reaction. Hence, solubility of NH_4Cl increases with rise in temperature.

- (b) Dissolution of sodium hydroxide in water



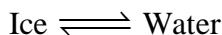
Sodium hydroxide dissolve in water with evolution of heat. Therefore, a rise in temperature will decrease its solubility. On the other hand, a decrease in temperature will increase the solubility of sodium hydroxide and reaction will shift in forward direction.

- (c) Effect of pressure on boiling point :



An increase in pressure will favour backward reaction i.e., the reaction in which volume decreases ($V_{\text{vap.}} > V_{\text{w.}}$). thus more water will exist at equilibrium (B.pt of solvent increase with increase in pressure). So decrease in pressure will shift the reaction forward.

- (d) Effect of pressure on melting point :

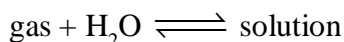


increase in pressure will favour forward reaction because $V_{\text{ice}} > V_{\text{water}}$. Thus more ice melt or the m.pt of ice is lowered with pressure.

For, $\text{Solid} \rightleftharpoons \text{Liquid}$

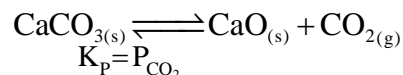
An increase in pressure will favour backward reaction because volume of liquid is more than solid thus more solid will exist at equilibrium (m.pt of solid increases with pressure).

- (e) Effect of pressure on solubility of gases :



increase in pressure favour forward reaction. [Henry's law]

- (f) In solid reactants equilibrium will not shift to the right side even if the more reactants are added.

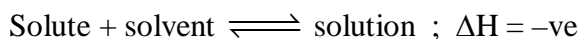


Equilibrium will not be affected by adding CaO or CaCO_3 at that temperature. But if volume is increased the equilibrium will shift to the right side to keep the pressure of CO_2 constant.

- (g) Effect of temperature on solubility



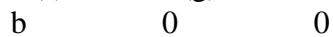
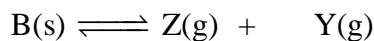
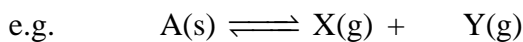
An increase in temperature favour endothermic or forward reaction i.e., solubility increases (urea, glucose).



In exothermic dissolution solubility decreases with temperature i.e., reaction will be in backward direction.

9. SIMULTANEOUS EQUILIBRIUM

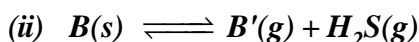
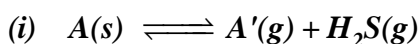
If in any container there are two or more equilibria existing simultaneously involving one or more than one common species, then in both/all the equilibrium, the concentration of common species is the total concentration of that species due to all the equilibria under consideration.



$$K_{C_1} = t(u + t)$$

$$K_{C_2} = (u + t)u$$

Ex.35 Two solid compounds A and B dissociate into gaseous products at 20°C as

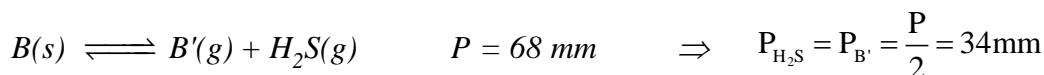
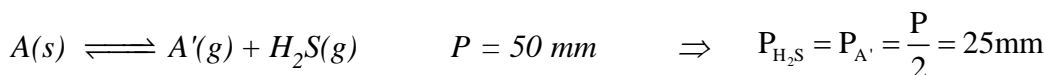
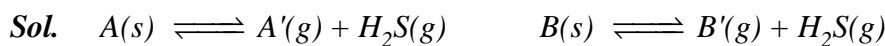


At 20°C, pressure over excess solid A is 50 mm and that over excess solid B is 68 mm find

(a) The dissociation constant of A and B

(b) Relative no. of moles of A and B in the vapour phase over a mixture of solid A and B.

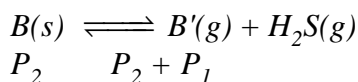
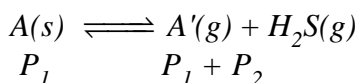
(c) Show that the total pressure of the gas over the solid mixture would be 84.4 mm



(i) $K_{P_1} = (25)^2 = 625 \text{ mm}^2$

$K_{P_2} = (34)^2 = 1156 \text{ mm}^2$

(ii) Ratio of moles is same as that of partial pressure so,



$K_{P_1} = P_{A'} \times P_{H_2S} = P_1(P_1 + P_2)$... (i)

$K_{P_2} = P_{B'} \times P_{H_2S} = P_2(P_1 + P_2)$... (ii)

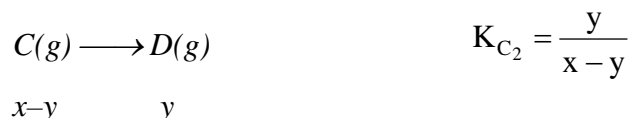
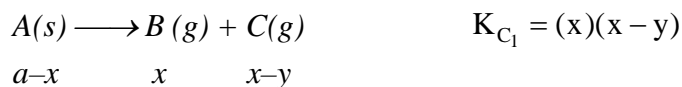
$$\frac{K_{P_1}}{K_{P_2}} = \frac{P_1}{P_2} = \frac{625}{1156}$$

(iii) total pressure = $P_1 + P_2 + (P_1 + P_2) = 2(P_1 + P_2)$

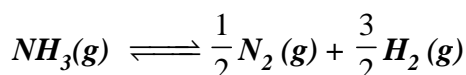
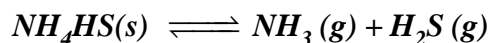
(i) + (ii) = $(P_1 + P_2)^2$

$\sqrt{K_{P_1} + K_{P_2}} = P_1 + P_2 \Rightarrow P_T = \sqrt{2(K_{P_1} + K_{P_2})} = 84.4 \text{ mm}$

10. SEQUENTIAL EQUILIBRIUM

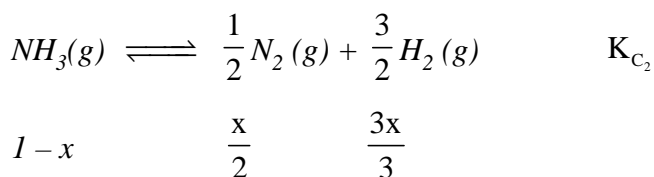
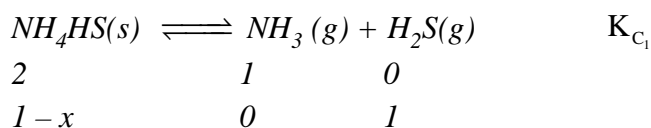


Ex36. 102 g of solid NH_4HS is taken in the 2L evacuated flask at $57^\circ C$. Following two equilibrium exist simultaneously



one mole of the solid decomposes to maintain both the equilibrium and 0.75 mole of H_2 was found at the equilibrium then find the equilibrium concentration of all the species and K_C for both the reaction.

Sol. Moles of $NH_4HS = \frac{102}{51} = 2$

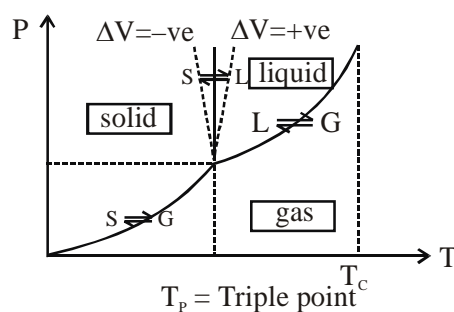


Given that moles of $H_2 = \frac{3x}{2} = 0.75 \Rightarrow x = \frac{1}{2}$

$$K_{C_1} = \frac{1}{2} \frac{(1-x)}{2} = \frac{1}{8} \quad [\text{Since } V = 2 L]$$

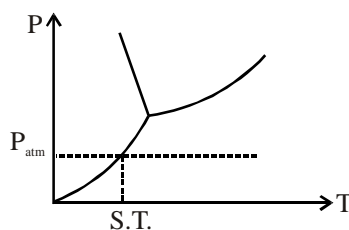
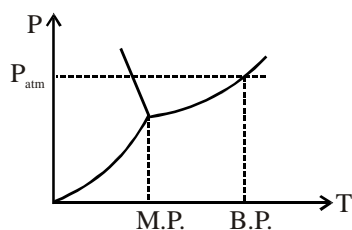
$$K_{C_3} = \frac{\left(\frac{3x}{4}\right)^{3/2} \left(\frac{x}{4}\right)^{1/2}}{\left(\frac{1-x}{2}\right)} = \frac{\left(\frac{3}{8}\right)^{3/2} \left(\frac{1}{4}\right)^{1/2}}{\left(\frac{1}{4}\right)} = (3)^{3/2} \frac{1}{64} \times \frac{4}{1} = \frac{(3)^{3/2}}{16}$$

11. PHYSICAL EQUILIBRIUM



- (i) The combination of temperature and pressure at which all the three physical state of matter co-exist is called triple point of that matter.
- (ii) The vapour pressure solid is minimum (0) at absolute zero and maximum at triple point.
- (iii) The vapour pressure of liquid is minimum at triple point and maximum at critical temperature.
- (iv) On each line in the graph, the matter exist in two physical states is equilibrium.
- (v) In between two lines, the matter exist in only one physical state.
- (vi) The melting point of solid and the triple point of matter differs slightly.
- (vii) Any solid may be directly converted into gaseous state or through liquid state by adjusting the external pressure relative to triple point pressure.

(viii)



EXERCISE # S-I

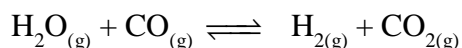
- Which of the following reactions goes almost all the way to completion, and which proceeds hardly at all?
 - $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}); \quad K_c = 2.7 \times 10^{-18}$
 - $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g}); \quad K_c = 6.0 \times 10^{13}$
- Write down the expression for equilibrium constant K_c and K_p for the following reactions :
 - $\text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g})$
 - $\text{H}_2\text{O}(\ell) \rightleftharpoons \text{H}_2\text{O}(\text{g})$
 - $\text{NH}_2\text{COONH}_4(\text{s}) \rightleftharpoons 2\text{NH}_3(\text{g}) + \text{CO}_2(\text{g})$
 - $\text{CH}_3\text{COOH}(\ell) + \text{C}_2\text{H}_5\text{OH}(\ell) \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5(\ell) + \text{H}_2\text{O}(\ell)$
 - $\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$
(excess)
 - $\text{Zn}(\text{s}) + 2\text{H}^+(\text{aq}) \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + \text{H}_2(\text{g})$
- Write the relationship between K_p and K_c for the following reactions :
 - $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
 - $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
 - $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$
 - $2\text{H}_2\text{O}(\text{g}) \rightleftharpoons 2\text{H}_2(\text{g}) + \text{O}_2(\text{g})$
 - $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$
- Find stability of reactants for the given equilibrium reaction :

$$2\text{XO}(\text{g}) \rightleftharpoons \text{X}_2(\text{g}) + \text{O}_2(\text{g}) \quad ; \quad K_1 = 1 \times 10^{24}$$

$$2\text{XO}_2(\text{g}) \rightleftharpoons \text{X}_2(\text{g}) + 2\text{O}_2(\text{g}) \quad ; \quad K_2 = 2.5 \times 10^{10}$$
- The value of K_c for the reaction $2\text{A} \rightleftharpoons \text{B} + \text{C}$ is 2×10^{-3} . At a given time, the composition of reaction mixture is $[\text{A}] = [\text{B}] = [\text{C}] = 3 \times 10^{-4} \text{ M}$. In which direction the reaction will proceed?
- The ester or ethyl acetate is formed by the reaction between ethanol and acetic acid and equilibrium is represented as :

$$\text{CH}_3\text{COOH}_{(\text{l})} + \text{C}_2\text{H}_5\text{OH}_{(\text{l})} \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5_{(\text{l})} + \text{H}_2\text{O}_{(\text{l})}$$
 - Write the concentration ratio (reaction quotient), Q_c for this reaction. (Note that water is not in excess and is not a solvent in this reaction).
 - At 293 K, if starts with 1.00 mole of acetic acid and 0.180 moles of ethanol, there is 0.171 moles of ethyl acetate in the final equilibrium mixture. Calculate the equilibrium constant.
 - Starting with 0.500 moles of ethanol and 1.000 mole of acetic acid and maintaining it at 293 K, 0.214 moles of ethyl acetate is found after some time. Has equilibrium been reached ?

7. If $K_c = 0.5 \times 10^{-9}$ at 1000 K for the reaction $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$, what is K_c at 1000 K for the reaction $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$?
8. An equilibrium mixture of PCl_5 , PCl_3 and Cl_2 at a certain temperature contains 0.5×10^{-3} M PCl_5 , 1.5×10^{-2} M PCl_3 , and 3×10^{-2} M Cl_2 . Calculate the equilibrium constant K_c for the reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$.
9. A sample of HI (9.6×10^{-3} mol) was placed in an empty 2.00 L container at 1000 K. After equilibrium was reached, the concentration of I_2 was 4×10^{-4} M. Calculate the value of K_c at 1000 K for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$.
10. The vapour pressure of water at 27°C is 0.2463 atm. Calculate the values of K_p and K_c at 27°C for the equilibrium $H_2O(l) \rightleftharpoons H_2O(g)$.
11. The value of K_c for the reaction $3O_2(g) \rightleftharpoons 2O_3(g)$ is 8×10^{-55} at 25°C . Do you expect pure air at 25°C to contain much O_3 (ozone) when O_2 and O_3 are in equilibrium? If the equilibrium concentration of O_2 in air at 25°C is 8×10^{-3} M, what is the equilibrium concentration of O_3 ?
12. One mole of H_2O and one mole of CO are taken in a 10 L vessel and heated to 725 K. At equilibrium 40 percent of water (by mass) reacts with carbon monoxide according to the equation.



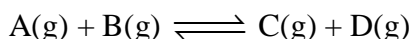
Calculate the equilibrium constant for the reaction.

13. A vessel at 1000 K contains CO_2 with a pressure of 0.6 atm. some of the CO_2 is converted into CO on addition of graphite. Calculate the value of K , if total pressure at equilibrium is 0.9 atm.
14. Calculate the equilibrium concentration of H_2 , I_2 and HI at 300 K if initially 2 mol of H_2 and I_2 are taken in a closed container of having volume 10 lit. [Given : $H_2 + I_2 \rightleftharpoons 2HI$; $K = 100$ at 300 K]
15. A mixture of SO_3 , SO_2 and O_2 gases is maintained at equilibrium in 10 litre flask at a particular temperature in which K_c for the reaction,
 $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ is $100 \text{ mol}^{-1} \text{ litre}$.

At equilibrium,

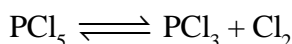
- (a) If number of mole of SO_3 and SO_2 in flask are same, how many mole of O_2 are present ?
- (b) If number of mole of SO_3 in flask are twice the number of mole of SO_2 , how many mole of O_2 are present ?

16. For the given reaction,



the number of moles at equilibrium was found to be 4, 4, 2 & 8 respectively in 1 L container. Find the new equilibrium concentration if 18 moles of D are added to above 1 L container.

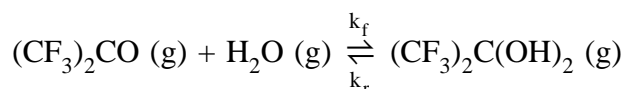
17. For the given reaction,



the number of moles at equilibrium was found to be 2, 6 & 4 respectively at 10 atm pressure. Find the new equilibrium moles & partial pressure, if it is reestablished at an equilibrium pressure 50 atm.

18. For the dissociation reaction $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ derive the expression for the degree of dissociation in terms of K_p and total pressure P .
19. For the reaction $2\text{SO}_{3(\text{g})} \rightleftharpoons 2\text{SO}_{2(\text{g})} + \text{O}_{2(\text{g})}$
Initially 5 moles of SO_3 is taken and at equilibrium 4 moles of SO_3 is dissociated then find out α and the value of K_c (Volume = 2 litre)
20. 1.1 mole of A mixed with 2.2 mole of B and the mixture is kept in a 1 litre flask at the equilibrium, $\text{A} + 2\text{B} \rightleftharpoons 2\text{C} + \text{D}$ is reached. At equilibrium 0.2 mole of C is formed then the value of K_c will be.
21. The air pollutant NO is produced in automobile engines from the high temperature reaction $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$; $K_c = 16$ at 2300 K. If the initial concentrations of N_2 and O_2 at 2300 K are both 1.5 M, what are the concentrations of NO, N_2 , and O_2 when the reaction mixture reaches equilibrium?
22. At 700 K, $K_p = 0.2$ for the reaction $\text{ClF}_3(\text{g}) \rightleftharpoons \text{ClF}(\text{g}) + \text{F}_2(\text{g})$. Calculate the equilibrium partial pressure of ClF_3 , ClF , and F_2 if only ClF_3 is present initially, at a partial pressure of 0.150 atm.
23. The degree of dissociation of N_2O_4 into NO_2 at 1.5 atmosphere and 40°C is 0.25. Calculate its K_p at 40°C . Also report degree of dissociation at 10 atmospheric pressure at same temperature.
24. At 46°C , K_p for the reaction $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ is 0.667 atm. Compute the percent dissociation of N_2O_4 at 46°C at a total pressure of 380 Torr.
25. $2\text{NOBr}(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}) + \text{Br}_2(\text{g})$. If nitrosyl bromide (NOBr) is 33.33% dissociated at 25°C & a total pressure of 0.28 atm. Calculate K_p for the dissociation at this temperature.
26. The system $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ maintained in a closed vessel at 60°C & a pressure of 5 atm has an average (i.e. observed) molecular weight of 69, calculate K_p . At what pressure at the same temperature would the observed molecular weight be (230/3)?
27. In the esterification $\text{C}_2\text{H}_5\text{OH}(\text{l}) + \text{CH}_3\text{COOH}(\text{l}) \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5(\text{l}) + \text{H}_2\text{O}(\text{l})$ an equimolar mixture of alcohol and acid taken initially yields under equilibrium, the water with mole fraction = 0.333. Calculate the equilibrium constant.
28. The equilibrium constant for the reaction is 9 at 900°C $\text{S}_2(\text{g}) + \text{C}(\text{s}) \rightleftharpoons \text{CS}_2(\text{g})$. Calculate the pressure of two gases at equilibrium, when 2 atm of S_2 and excess of $\text{C}(\text{s})$ come to equilibrium.
29. A sample of $\text{CaCO}_3(\text{s})$ is introduced into a sealed container of volume 0.821 litre & heated to 1000K until equilibrium is reached. The equilibrium constant for the reaction $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ is 4×10^{-2} atm at this temperature. Calculate the mass of CaO present at equilibrium.

30. Anhydrous calcium chloride is often used as a desiccant. In the presence of excess of CaCl_2 , the amount of the water taken up is governed by $K_p = 6.4 \times 10^{85}$ for the following reaction at room temperature, $\text{CaCl}_2(\text{s}) + 6\text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CaCl}_2 \cdot 6\text{H}_2\text{O}(\text{s})$. What is the equilibrium vapour pressure of water in a closed vessel that contains $\text{CaCl}_2(\text{s})$?
31. 20.0 grams of $\text{CaCO}_3(\text{s})$ were placed in a closed vessel, heated & maintained at 727°C under equilibrium $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ and it is found that 75 % of CaCO_3 was decomposed. What is the value of K_p ? The volume of the container was 15 litres.
- 32.(a) Methanol, a liquid fuel that could possibly replace gasoline, can be prepared from water gas and additional hydrogen at high temperature and pressure in the presence of a suitable catalyst. Write the expression for the equilibrium constant for the reversible reaction.
- $$2\text{H}_2(\text{g}) + \text{CO}(\text{g}) \rightleftharpoons \text{CH}_3\text{OH}(\text{g}) \quad \Delta H = -90.2 \text{ kJ}$$
- (b) Assume that equilibrium has been established and predict how the concentration of H_2 , CO and CH_3OH will differ at a new equilibrium if (1) more H_2 is added. (2) CO is removed. (3) CH_3OH is added. (4) the pressure on the system is increased. (5) the temperature of the system is increased. (6) more catalyst is added.
33. Ammonia is a weak base that reacts with water according to the equation
- $$\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+ + \text{OH}^-(\text{aq})$$
- Will any of the following increase the percent of ammonia that is converted to the ammonium ion in water?
- (a) Addition of NaOH . (b) Addition of HCl . (c) Addition of NH_4Cl .
34. Consider the gas-phase hydration of hexafluoroacetone, $(\text{CF}_3)_2\text{CO}$:



At 76°C , the forward and reverse rate constants are $k_f = 0.15 \text{ M}^{-1}\text{s}^{-1}$ and $k_r = 6 \times 10^{-4}\text{s}^{-1}$. What is the value of the equilibrium constant K_c ?

35. Listed in the table are forward and reverse rate constants for the reaction $2\text{NO}(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + \text{O}_2(\text{g})$

Temperature (K)	$k_f (\text{M}^{-1}\text{s}^{-1})$	$k_r (\text{M}^{-1}\text{s}^{-1})$
1400	0.29	1.1×10^{-6}
1500	1.3	1.4×10^{-5}

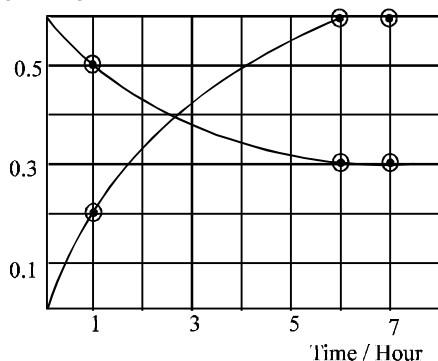
Is the reaction endothermic or exothermic? Explain in terms of kinetics.

EXERCISE # S-II

- One mole of $\text{N}_2\text{O}_4(\text{g})$ at 300 K is left in a closed container under one atm. It is heated to 600 K when 20 % by mass of $\text{N}_2\text{O}_4(\text{g})$ decomposes to $\text{NO}_2(\text{g})$. Calculate resultant pressure.
- Solid Ammonium carbamate dissociates as: $\text{NH}_2\text{COONH}_4(\text{s}) \rightleftharpoons 2\text{NH}_3(\text{g}) + \text{CO}_2(\text{g})$. In a closed vessel solid ammonium carbamate is in equilibrium with its dissociation products. At equilibrium, ammonia is added such that the partial pressure of NH_3 at new equilibrium now equals the original total pressure. Calculate the ratio of total pressure at new equilibrium to that of original total pressure.
- A definite amount of solid NH_4HS is placed in a flask already containing ammonia gas at a certain temperature and 0.50 atm pressure. NH_4HS decomposes to give NH_3 and H_2S and at equilibrium total pressure in flask is 0.84 atm. Calculate equilibrium constant for the reaction :
- For the reaction $\text{A}(\text{g}) + 2\text{B}(\text{g}) \rightleftharpoons \text{C}(\text{g}) + \text{D}(\text{g})$; $K_c = 10^{12}$.
If the initial moles of A,B,C and D are 0.5, 1, 0.5 and 3.5 moles respectively in a one litre vessel. What is the equilibrium concentration of B?
- Calculate the equilibrium concentration of PCl_3 and Cl_2 at 300 K if initially 1 mol of PCl_5 is taken in a closed container of having volume 10 lit.
[Given : $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$; $K_c = 10^{-2}$ at 300 K]
- When 36.8g $\text{N}_2\text{O}_4(\text{g})$ is introduced into a 1.0-litre flask at 27°C . The following equilibrium reaction occurs : $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$; $K_p = 0.1642$ atm.
 - Calculate K_c of the equilibrium reaction.
 - What are the number of moles of N_2O_4 and NO_2 at equilibrium?
 - What is the total gas pressure in the flask at equilibrium?
 - What is the percent dissociation of N_2O_4 ?
- The progress of the reaction

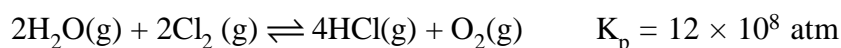
$\text{A} \rightleftharpoons n\text{B}$ with time, is presented in figure. Determine

- the value of n.
- the equilibrium constant K.
- the initial rate of conversion of A.



- A mixture of hydrogen & iodine in the mole ratio 1.5 : 1 is maintained at 450°C . After the attainment of equilibrium $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$, it is found on analysis that the mole ratio of I_2 to HI is 1 : 18. Calculate the equilibrium constant and the number of moles of each species present under equilibrium, if initially, 127 grams of iodine were taken.

9. At certain temperature (T) for the gas phase reaction



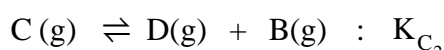
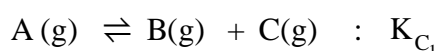
If Cl_2 , HCl & O_2 are mixed in such a manner that the partial pressure of each is 2 atm and the mixture is brought into contact with excess of liquid water. What would be approximate partial pressure of Cl_2 when equilibrium is attained at temperature (T)?

[Given : Vapour pressure of water is 380 mm Hg at temperature (T)]

10. Two solids X and Y dissociate into gaseous products at a certain temperature as follows:

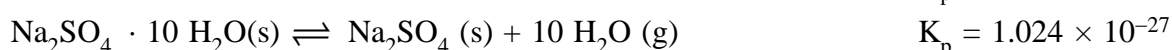
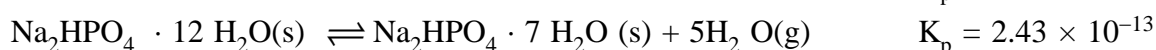
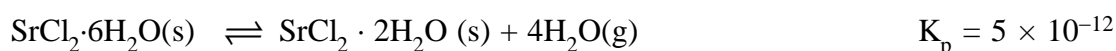
$\text{X(s)} \rightleftharpoons \text{A(g)} + \text{C(g)}$, and $\text{Y(s)} \rightleftharpoons \text{B(g)} + \text{C(g)}$. At a given temperature, pressure over excess solid X is 40 mm and total pressure over solid Y is 60 mm. When they are preset in separate containers. Calculate

- the values of K_p for two reactions (in mm^2)
 - the ratio of moles of A and B in the vapour state over a mixture of X and Y.
 - the total pressure of gases over a mixture of X and Y.
11. When 1 mole of A(g) is introduced in a closed rigid 1 litre vessel maintained at constant temperature the following equilibria are established.



The pressure at equilibrium is twice the initial pressure. Calculate the value of $\frac{K_{C_2}}{K_{C_1}}$ if $\frac{[\text{C}]_{\text{eq}}}{[\text{B}]_{\text{eq}}} = \frac{1}{5}$

12. Equilibrium constants are given (in atm) for the following reactions at 0°C :



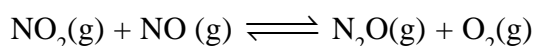
$$(\% \text{ Relative humidity} = \frac{P_{\text{H}_2\text{O}}}{\text{Vapour pressure of H}_2\text{O}} \times 100)$$

The vapor pressure of water at 0°C is 4.56 torr.

Out of $\text{SrCl}_2 \cdot 2\text{H}_2\text{O(s)}$, $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O(s)}$ and $\text{Na}_2\text{SO}_4(\text{s})$,

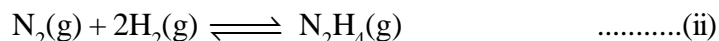
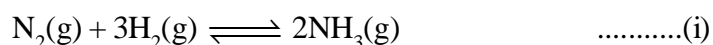
Which is the most effective drying agent at 0°C ?

13. At certain temperature, $K_C = 1.0$ for reaction :



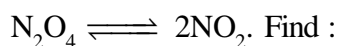
equal moles of NO and NO_2 are to be placed in 5 litre container until N_2O concentration at equilibrium is 0.5M. How many mole of $(\text{NO} + \text{NO}_2)$ must be placed in the container.

14. In a vessel, two equilibrium are simultaneously established at same temperature as follows,



Initially the vessel contains N_2 and H_2 in the molar ratio of 9 : 13. The equilibrium pressure is $7 P_0$ in which pressure due to ammonia is P_0 and due to hydrogen is $2P_0$. Find the values of equilibrium constants (K_p 's) for both the reactions.

15. If vapour density of equilibrium mixture NO_2 and N_2O_4 is found to be 42 for the reaction,



- (a) Abnormal molecular weight
- (b) Degree of dissociation
- (c) Percentage of NO_2 in the mixture

EXERCISE # O-I

Only one is correct

- $x \rightleftharpoons y$ reaction is said to be in equilibrium, when :-

(A) Only 10% conversion of x to y takes place
 (B) Complete conversion of x to y has taken place
 (C) Conversion of x to y is only 50% complete
 (D) The rate of change of x to y is just equal to the rate of change of y to x in the system
- For which reaction is $K_p = K_c$:-

(A) $2\text{NOCl(g)} \rightleftharpoons 2\text{NO(g)} + \text{Cl}_2\text{(g)}$ (B) $\text{N}_2\text{(g)} + 3\text{H}_2\text{(g)} \rightleftharpoons 2\text{NH}_3\text{(g)}$
 (C) $\text{H}_2\text{(g)} + \text{I}_2\text{(g)} \rightleftharpoons 2\text{HI(g)}$ (D) $2\text{SO}_2\text{(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2\text{SO}_3\text{(g)}$
- For the reaction

$$\text{CuSO}_4 \cdot 5\text{H}_2\text{O(s)} \rightleftharpoons \text{CuSO}_4 \cdot 3\text{H}_2\text{O(s)} + 2\text{H}_2\text{O(g)}$$

Which one is correct representation :-

(A) $K_p = (P_{\text{H}_2\text{O}})^2$ (B) $K_c = [\text{H}_2\text{O}]^2$ (C) $K_p = K_c(RT)^2$ (D) All
- $\log \frac{K_p}{K_c} + \log RT = 0$ is true relationship for the following reaction:-

(A) $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$ (B) $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$
 (C) $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ (D) (B) and (C) both
- For a reaction $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$, the value of K_c does not depends upon :-

(a) Initial concentration of the reactants (b) Pressure
 (c) Temperature (d) Catalyst
 (A) Only c (B) a, b, c (C) a, b, d (D) a, b, c, d
- If some He gas is introduced into the equilibrium $\text{PCl}_{5\text{(g)}} \rightleftharpoons \text{PCl}_{3\text{(g)}} + \text{Cl}_{2\text{(g)}}$ at constant pressure and temperature then equilibrium constant of reaction:

(A) Increase (B) Decrease (C) Unchange (D) Nothing can be said
- The equilibrium constant for the given reaction :

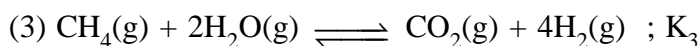
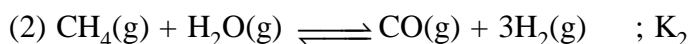
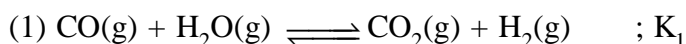
$$\text{SO}_3\text{(g)} \rightleftharpoons \text{SO}_2\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)} ; K_c = 5 \times 10^{-2}$$

The value of K_c for the reaction :

$$2\text{SO}_2\text{(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2\text{SO}_3\text{(g)}, \text{ will be}$$

(A) 400 (B) 2.40×10^{-3} (C) 9.8×10^{-2} (D) 4.9×10^{-2}

8. For the following three reactions, 1, 2 and 3 equilibrium, constants are given :



Which of the following relations is correct ?

(A) $K_1\sqrt{K_2} = K_3$ (B) $K_2K_3 = K_1$ (C) $K_3 = K_1K_2$ (D) $K_3 = K_2^3 K_1^2$

9. Sulfide ion in alkaline solution reacts with solid sulfur to form polysulfide ions having formulas S_2^{2-} , S_3^{2-} , S_4^{2-} and so on. The equilibrium constant for the formation of S_2^{2-} is 12 (K_1) & for the formation of S_3^{2-} is 132 (K_2), both from S and S^{2-} . What is the equilibrium constant for the formation of S_3^{2-} from S_2^{2-} and S?

(A) 11 (B) 12 (C) 132 (D) None of these

10. If 0.5 mole H_2 is reacted with 0.5 mole I_2 in a ten-litre container at 444°C and at same temperature value of equilibrium constant K_c is 49, the ratio of $[\text{HI}]$ and $[\text{I}_2]$ will be :-

(A) 7 (B) $\frac{1}{7}$ (C) $\sqrt{\frac{1}{7}}$ (D) 49

11. In the reaction, $\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO}$, the moles/litre of N_2 , O_2 and NO respectively 0.25, 0.05 and 1.0 at equilibrium. The initial concentrations of N_2 and O_2 will respectively be

(A) 0.75 mole/lit., 0.55 mole/lit. (B) 0.50 mole/lit., 0.75 mole/lit.
(C) 0.25 mole/lit., 0.50 mole/lit (D) 0.25 mole/lit., 1.0 mole/lit.

12. How many moles per litre of PCl_5 has to be taken to obtain 0.1 mole Cl_2 , if the value of equilibrium constant K_c is 0.04 ?

(A) 0.15 (B) 0.25 (C) 0.35 (D) 0.05

13. In the beginning of the reaction, $\text{A} \rightleftharpoons \text{B} + \text{C}$, 2 moles of A are taken, out of which 0.5 mole gets dissociated. What is the amount of dissociation of A ?

(A) 0.5 (B) 1 (C) 0.25 (D) 4.2

14. In the reaction, $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$, the amount of each PCl_5 , PCl_3 and Cl_2 is 2 mole at equilibrium and total pressure is 3 atmosphere. The value of K_p will be

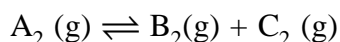
(A) 1.0 atm. (B) 3.0 atm. (C) 2.9 atm. (D) 6.0 atm.

15. 4 moles of PCl_5 are heated at constant temperature in closed container. If degree of dissociation for PCl_5 is 0.5 calculate total number of moles at equilibrium :-

(A) 4.5 (B) 6 (C) 3 (D) 4

16. For the reaction $A + 2B \rightleftharpoons 2C + D$, initial concentration of A is a and that of B is 1.5 times that of A. Concentration of A and D are same at equilibrium. What should be the concentration of B at equilibrium?
- (A) $\frac{a}{4}$ (B) $\frac{a}{2}$ (C) $\frac{3a}{4}$ (D) All of the above.
17. For the reaction $3A(g) + B(g) \rightleftharpoons 2C(g)$ at a given temperature, $K_c = 9.0$. What must be the volume of the flask, if a mixture of 2.0 mol each of A, B and C exist in equilibrium?
- (A) 6L (B) 9L (C) 36 L (D) None of these
18. For the following gases equilibrium. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
 K_p is found to be equal to K_c . This is attained when temperature is
- (A) 0°C (B) 273 K (C) 1 K (D) 12.19 K
19. The degree of dissociation of SO_3 is α at equilibrium pressure p^0 .
 K_p for $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$
- (A) $\frac{p^0 \alpha^3}{2(1-\alpha)^3}$ (B) $\frac{p^0 \alpha^3}{(2+\alpha)(1-\alpha)^2}$ (C) $\frac{p^0 \alpha^2}{2(1-\alpha)^2}$ (D) None of these
20. For the reaction: $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$, the degree of dissociated (α) of $HI(g)$ is related to equilibrium constant K_p by the expression
- (A) $\frac{1+2\sqrt{K_p}}{2}$ (B) $\sqrt{\frac{1+2K_p}{2}}$ (C) $\sqrt{\frac{2K_p}{1+2K_p}}$ (D) $\frac{2\sqrt{K_p}}{1+2\sqrt{K_p}}$
21. The equilibrium constant for the reaction
 $A(g) + 2B(g) \rightleftharpoons C(g)$
 is $0.25 \text{ dm}^6\text{mol}^{-2}$. In a volume of 5 dm^3 , what amount of A must be mixed with 4 mol of B to yield 1 mol of C at equilibrium.
- (A) 3 moles (B) 24 moles (C) 26 moles (D) None of these
22. A 20.0 litre vessel initially contains 0.50 mole each of H_2 and I_2 gases. These substances react and finally reach an equilibrium condition. Calculate the equilibrium concentration of HI if $K_{eq} = 49$ for the reaction $H_2 + I_2 \rightleftharpoons 2HI$.
- (A) 0.78 M (B) 0.039 M (C) 0.033 M (D) 0.021 M
23. At 675 K, $H_2(g)$ and $CO_2(g)$ react to form $CO(g)$ and $H_2O(g)$, K_p for the reaction is 0.16. If a mixture of 0.25 mole of $H_2(g)$ and 0.25 mol of CO_2 is heated at 675 K, mole % of $CO(g)$ in equilibrium mixture is :
- (A) 7.14 (B) 14.28 (C) 28.57 (D) 33.33
24. The vapour density of N_2O_4 at a certain temperature is 30. What is the % dissociation of N_2O_4 at this temperature?
- (A) 53.3% (B) 106.6% (C) 26.7% (D) None

25. The equilibrium constant K_p (in atm) for the reaction is 9 at 7 atm and 300 K.



Calculate the average molar mass (in gm/mol) of an equilibrium mixture.

Given : Molar mass of A_2 , B_2 and C_2 are 70, 49 & 21 gm/mol respectively.

- (A) 50 (B) 45 (C) 40 (D) 37.5
26. Vapour density of the equilibrium mixture of the reaction
 $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ is 6.0
 Percent dissociation of ammonia gas is:
 (A) 13.88 (B) 58.82 (C) 41.66 (D) None of these
27. The equilibrium concentration of B $[B]_e$ for the reversible reaction $A \rightleftharpoons B$ can be evaluated by the expression:-

- (A) $K_c[A]_e^{-1}$ (B) $\frac{k_f}{k_b}[A]_e^{-1}$ (C) $k_f k_b^{-1} [A]_e$ (D) $k_f k_b [A]^{-1}$

28. The equilibrium $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ shifts forward if :-

- (A) A catalyst is used.
 (B) An adsorbent is used to remove SO_3 as soon as it is formed.
 (C) Small amounts of reactants are removed.
 (D) None of these

29. In manufacture of NO, the reaction $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$, ΔH +ve is favourable if :-

- (A) Pressure is increased (B) Pressure is decreased
 (C) Temperature is increased (D) Temperature is decreased

30. In which of the following reactions, increase in the pressure at constant temperature does not affect the moles at equilibrium :

- (A) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ (B) $C(g) + \frac{1}{2}O_2(g) \rightleftharpoons CO(g)$
 (C) $H_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons H_2O(g)$ (D) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

31. Change in volume of the system does not alter the number of moles in which of the following equilibrium

- (A) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ (B) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
 (C) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ (D) $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$

32. The conditions favourable for the reaction :



are :

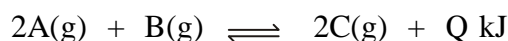
- (A) low temperature, high pressure
 (B) any value of T and P
 (C) low temperature and low pressure
 (D) high temperature and high pressure

33. Densities of diamond and graphite are 3.5 and 2.3 gm/mL.



favourable conditions for formation of diamond are

- (A) high pressure and low temperature
 - (B) low pressure and high temperature
 - (C) high pressure and high temperature
 - (D) low pressure and low temperature
34. The equilibrium $\text{SO}_2\text{Cl}_2(\text{g}) \rightleftharpoons \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$ is attained at 25°C in a closed rigid container and an inert gas, helium is introduced. Which of the following statements is/are correct.
- (A) concentrations of SO_2 , Cl_2 and SO_2Cl_2 do not change
 - (B) more chlorine is formed
 - (C) concentration of SO_2 is reduced
 - (D) more SO_2Cl_2 is formed
35. The yield of product in the reaction



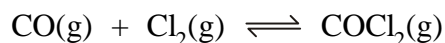
would be lower at :

- (A) low temperature and low pressure
- (B) high temperature & high pressure
- (C) low temperature and to high pressure
- (D) high temperature & low pressure

EXERCISE # O-II

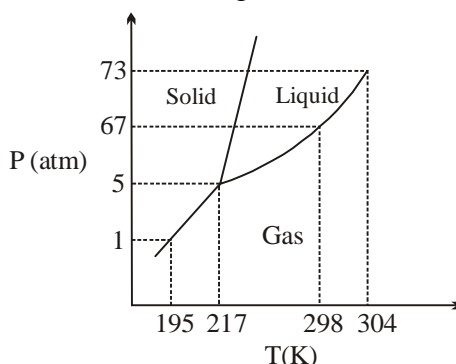
More than one may be correct

1. Following two equilibrium is simultaneously established in a container



If some Ni(s) is introduced in the container forming $\text{Ni}(\text{CO})_4(\text{g})$ then at new equilibrium

- (A) PCl_3 concentration will increase (B) PCl_3 concentration will decrease
(C) Cl_2 concentration will remain same (D) CO concentration will remain same
2. For the reaction $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$, the forward reaction at constant temperature is favoured by
(A) introducing an inert gas at constant volume
(B) introducing chlorine gas at constant volume
(C) introducing an inert gas at constant pressure
(D) introducing PCl_5 at constant volume.
3. When NaNO_3 is heated in a closed vessel, oxygen is liberated and NaNO_2 is left. At equilibrium
(A) addition of NaNO_2 favours reverse reaction
(B) addition of NaNO_3 favours forward reaction
(C) increasing temperature favours forward reaction
(D) increasing pressure favours reverse reaction
4. For the gas phase reaction, $\text{C}_2\text{H}_4 + \text{H}_2 \rightleftharpoons \text{C}_2\text{H}_6$ ($\Delta H = -32.7 \text{ kcal}$), carried out in a closed vessel, the equilibrium moles of C_2H_4 can be increased by
(A) increasing the temperature (B) decreasing the pressure
(C) removing some H_2 (D) adding some C_2H_6
5. Phase diagram of CO_2 is shown as following



Based on above find the correct statement(s)

- (A) 298K is the normal boiling point of liquid CO_2
(B) At 1 atm & 190 K CO_2 will exist as gas.
(C) $\text{CO}_2(\text{s})$ will sublime above 195K under normal atmospheric pressure
(D) Melting point & boiling point of CO_2 will increase on increasing pressure

6. The equilibrium between, gaseous isomers A, B and C can be represented as

Reaction	Equilibrium constant
$A(g) \rightleftharpoons B(g)$	$K_1 = ?$
$B(g) \rightleftharpoons C(g)$	$K_2 = 0.4$
$C(g) \rightleftharpoons A(g)$	$K_3 = 0.6$

If one mole of A is taken in a closed vessel of volume 1 litre, then

- (A) $[A] + [B] + [C] = 1$ M at any time of the reactions
 (B) Concentration of C is 4.1 M at the attainment equilibrium in all the reactions
 (C) The value of K_1 is $\frac{1}{0.24}$
 (D) Isomer [A] is least stable as per thermodynamics.
7. For the gas phase exothermic reaction, $A_2 + B_2 \rightleftharpoons C_2$, carried out in a closed vessel, the equilibrium moles of A_2 can be increased by
 (A) increasing the temperature (B) decreasing the pressure
 (C) adding inert gas at constant pressure (D) removing some C_2
8. Consider the equilibrium $HgO(s) + 4I^-(aq) + H_2O(l) \rightleftharpoons HgI_4^{2-}(aq) + 2OH^-(aq)$, which changes will decrease the equilibrium concentration of HgI_4^{2-}
 (A) Addition of 0.1 M HI (aq) (B) Addition of HgO (s)
 (C) Addition of $H_2O(l)$ (D) Addition of KOH (aq)
9. Decrease in the pressure for the following equilibria : $H_2O(s) \rightleftharpoons H_2O(l)$ result in the :
 (A) formation of more $H_2O(s)$ (B) formation of more $H_2O(l)$
 (C) increase in melting point of $H_2O(s)$ (D) decrease in melting point of $H_2O(s)$

Assertion Reason

10. **Statement -1** : Total number of moles in a closed system at new equilibrium is less than the old equilibrium if some amount of a substance is removed from a system
 (consider a reaction $A(g) \rightleftharpoons B(g)$) at equilibrium.
Statement -2 : The number of moles of the substance which is removed, is partially compensated as the system reached to new equilibrium.
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
 (C) Statement-1 is false, statement-2 is true.
 (D) Statement-1 is true, statement-2 is false.
11. **Statement-1** : Ammonia at a pressure of 10 atm and CO_2 at a pressure of 20 atm are introduced into an evacuated chamber. If K_p for the reaction
 $NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$ is 2020 atm^3 , the total pressure after a long time is less than 30 atm.
Statement-2 : Equilibrium can be attained from both directions.
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
 (C) Statement-1 is true, statement-2 is false.
 (D) Statement-1 is false, statement-2 is true.

12. **Statement-1** : Catalyst does not alter the equilibrium constant
Statement-2 : Because for the catalysed reaction and uncatalysed reaction ΔH remain same an equilibrium constant depend on ΔH .
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
 (C) Statement-1 is true, statement-2 is false.
 (D) Statement-1 is false, statement-2 is true.
13. **Statement-1** : Equilibrium constant may show higher or lower values with increase in temperature
Statement-2 : The change depend on heat of reaction.
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
 (C) Statement-1 is true, statement-2 is false.
 (D) Statement-1 is false, statement-2 is true.

Comprehension :

Paragraph for Question Nos. 12 to 15

In a 7.0 L evacuated chamber, 0.50 mol H_2 and 0.50 mol I_2 react at $427^\circ C$.

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$. At the given temperature, $K_C = 49$ for the reaction.

14. What is the value of K_p ?
 (A) 7 (B) 49 (C) 24.5 (D) None
15. What is the total pressure (atm) in the chamber?
 (A) 83.14 (B) 831.4 (C) 8.21 (D) None
16. How many moles of the iodine remain unreacted at equilibrium?
 (A) 0.388 (B) 0.112 (C) 0.25 (D) 0.125
17. What is the partial pressure (atm) of HI in the equilibrium mixture?
 (A) 6.385 (B) 12.77 (C) 40.768 (D) 646.58

Paragraph for Question Nos. 16 to 18

Influence of pressure, temperature, concentration and addition of inert gas on a reversible chemical reaction in equilibrium can be explained by formulating the expression for equilibrium constant K_c or K_p for the equilibrium. On the other hand Le Chatelier principle can be theoretically used to explain the effect of P, T or concentration on the physical or chemical equilibrium both.

18. For the reaction : $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ increase of pressure shows :
 (A) An increase in degree of dissociation and a decrease in K_c
 (B) A decrease in degree of dissociation and a decrease in K_c
 (C) An increase in degree of dissociation but K_c remains constant
 (D) A decrease in degree of dissociation but K_c remains constant
19. For the reaction : $2SO_2 + O_2 \rightleftharpoons 2SO_3$; $\Delta H = -ve$, An increase in temperature shows :
 (A) More dissociation of SO_3 and a decrease in K_c
 (B) Less dissociation of SO_3 and an increase in K_c
 (C) More dissociation of SO_3 and an increase in K_c
 (D) Less dissociation of SO_3 and an decrease in K_c

20. For the reaction : $\underset{\text{Yellow}}{\text{Fe}^{3+}(\text{aq.})} + \text{SCN}^{-}(\text{aq.}) \rightleftharpoons \underset{\text{Red}}{[\text{Fe}(\text{NCS})]^{2+}(\text{aq.})}$; in equilibrium if little more aqueous solution

of FeCl_3 is added, than :

- (A) Forward reaction becomes more and red colour is deepened
 (B) Backward reaction becomes more and red colour faintens
 (C) Solution becomes colourless
 (D) None of these

Match the column :

- | 21. | Column I | Column II |
|-----|---|--|
| (A) | $K_p < K_c$ | (P) $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ |
| (B) | Introduction of inert gas at constant pressure will decrease the concentration of reactants | (Q) $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ |
| (C) | K_p° is dimensionless | (R) $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$ |
| (D) | Temperature increase will shift the reaction on product side. | (S) $\text{NH}_3(\text{g}) + \text{HI}(\text{g}) \rightleftharpoons \text{NH}_4\text{I}(\text{s})$ |

- | 22. | Column-I
(Reactions) | Column-II
(Favourable conditions) |
|-----|---|--|
| (A) | Oxidation of nitrogen
$\text{N}_2(\text{g}) + \text{O}_2(\text{g}) + 180.5 \text{ kJ} \rightleftharpoons 2\text{NO}(\text{g})$ | (p) Addition of inert gas at constant pressure |
| (B) | Dissociation of $\text{N}_2\text{O}_4(\text{g})$
$\text{N}_2\text{O}_4(\text{g}) + 57.2 \text{ kJ} \rightleftharpoons 2\text{NO}_2(\text{g})$ | (q) Decrease in pressure |
| (C) | Oxidation of $\text{NH}_3(\text{g})$
$4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightleftharpoons 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g}) + 905.6 \text{ kJ}$ | (r) Decrease in temperature |
| (D) | Formation of $\text{NO}_2(\text{g})$
$\text{NO}(\text{g}) + \text{O}_3(\text{g}) \rightleftharpoons \text{NO}_2(\text{g}) + \text{O}_2(\text{g}) + 200 \text{ kJ}$ | (s) Increase in temperature |

Matching list type :

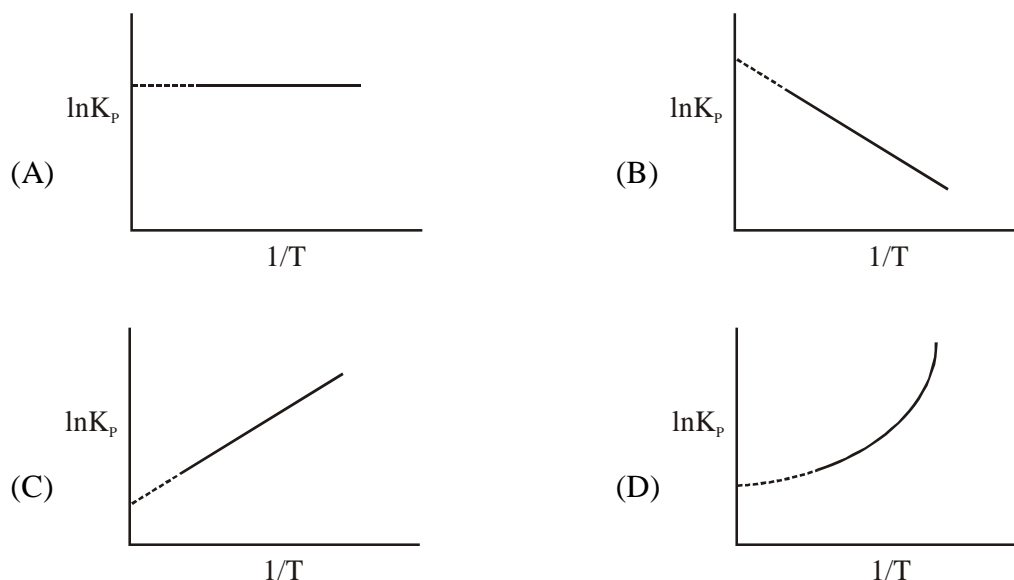
Answer Q.No. 23, 24 and 25 by appropriately matching the information given in the three columns of the following table.

Column-I (Reaction)	Column-II (If α is negligible w.r.t. 1)	Column-III
(A) $2X(g) \rightleftharpoons Y(g) + Z(g), \Delta H = -ve$	(P) $\alpha = 2 \times \sqrt{K_p}$	(I) K increase with increase in temperature
(B) $X(g) \rightleftharpoons Y(g) + Z(g), \Delta H = +ve$	(Q) $\alpha = 3 \times \sqrt{K_p}$	(II) K decrease with increase in temperature
(C) $3X(g) \rightleftharpoons Y(g) + Z(g), \Delta H = +ve$	(R) $\alpha = (2K_p)^{1/3}$	(III) Pressure has no effect
(D) $2X(g) \rightleftharpoons Y(g) + 2Z(g), \Delta H = +ve$	(S) $\alpha = \sqrt{K_p}$	(IV) Addition of inert gas at constant pressure shift equilibrium in forward direction

23. Which of the following option is correctly matched ?

- (A) A-Q-III (B) B-S-II (C) C-Q-II (D) D-R-IV

24. Correct representation of reaction in option (A) is represented by graph



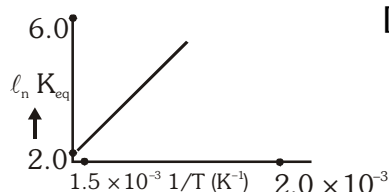
25. For the reaction of option (B) if degree of dissociation varies inversely as square root of pressure of the system. Suppose at constant temperature volume is increased 16 times of its initial volume the degree of dissociation (α) for this reaction will become :

- (A) 4 times (B) 2 times (C) 1/4 times (D) 1/2 times

EXERCISE : J-MAIN

1. One of the following equilibrium is not affected by change in volume of the flask - [AIEEE-2002]
 (1) $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ (2) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
 (3) $\text{N}_2(\text{g}) + \text{O}_2 \rightleftharpoons 2\text{NO}(\text{g})$ (4) $\text{SO}_2\text{Cl}_2(\text{g}) \rightleftharpoons \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$
2. Reaction $\text{CO}_{(\text{g})} + \frac{1}{2} \text{O}_{2(\text{g})} \rightleftharpoons \text{CO}_{2(\text{g})}$. The value of $\frac{K_p}{K_c}$ is - [AIEEE-2002]
 (1) $\frac{1}{RT}$ (2) \sqrt{RT} (3) $\frac{1}{\sqrt{RT}}$ (4) RT
3. Consider the reaction equilibrium [AIEEE-2003]
 $2\text{SO}_{2(\text{g})} + \text{O}_{2(\text{g})} \rightleftharpoons 2\text{SO}_{3(\text{g})}$; $\Delta H^\circ = -198 \text{ kJ}$
 On the basis of Le-Chatelier's principle, the condition favourable for the forward reaction is -
 (1) Lowering the temperature and increasing the pressure
 (2) Any value of temperature as well as pressure
 (3) Lowering of temperature as well as pressure
 (4) Increasing temperature as well as pressure
4. For the reaction equilibrium,
 $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ the concentration of N_2O_4 and NO_2 at equilibrium are 4.8×10^{-2} and $1.2 \times 10^{-2} \text{ mol L}^{-1}$ respectively. The value of K_c for the reaction is- [AIEEE-2003]
 (1) $3 \times 10^{-3} \text{ mol L}^{-1}$ (2) $3 \times 10^3 \text{ mol L}^{-1}$
 (3) $3.3 \times 10^2 \text{ mol L}^{-1}$ (4) $3 \times 10^{-1} \text{ mol L}^{-1}$
5. The equilibrium constant for the reaction
 $\text{N}_{2(\text{g})} + \text{O}_{2(\text{g})} \rightleftharpoons 2\text{NO}_{(\text{g})}$ at temperature T is 4×10^{-4} . The value of K_c for the reaction
 $\text{NO}_{(\text{g})} \rightleftharpoons \frac{1}{2} \text{N}_{2(\text{g})} + \frac{1}{2} \text{O}_{2(\text{g})}$ [AIEEE-2004]
 (1) 2.5×10^2 (2) 50 (3) 4×10^{-4} (4) 0.02
6. For the reaction $\text{CO}_{(\text{g})} + \text{Cl}_{2(\text{g})} \rightleftharpoons \text{COCl}_{2(\text{g})}$ the $\frac{K_p}{K_c}$ is equal to - [AIEEE-2004]
 (1) $\frac{1}{RT}$ (2) RT (3) \sqrt{RT} (4) 1.0
7. What is the equilibrium expression for the reaction $\text{P}_{4(\text{s})} + 5\text{O}_{2(\text{g})} \rightleftharpoons \text{P}_4\text{O}_{10(\text{s})}$? [AIEEE-2004]
 (1) $K_c = [\text{P}_4\text{O}_{10}] / [\text{P}_4] [\text{O}_2]^5$ (2) $K_c = [\text{P}_4\text{O}_{10}] / 5 [\text{P}_4] [\text{O}_2]$
 (3) $K_c = [\text{O}_2]^5$ (4) $K_c = 1 / [\text{O}_2]^5$

8. A schematic plot of $\ln K_{eq}$ versus inverse of temperature for a reaction is shown below. The reaction must be [AIEEE-2005]



- (1) endothermic
(2) exothermic
(3) highly spontaneous at ordinary temperature
(4) one with negligible enthalpy change

9. The exothermic formation of ClF_3 is represented by the equation [AIEEE-2005]



Which of the following will increase the quantity of ClF_3 in an equilibrium mixture of Cl_2 , F_2 and ClF_3 ?

- (1) Removing Cl_2 (2) Increasing the temperature
(3) Adding F_2 (4) Increasing the volume of the container

10. For the reaction $2\text{NO}_{2(g)} \rightleftharpoons 2\text{NO}_{(g)} + \text{O}_{2(g)}$, ($K_c = 1.8 \times 10^{-6}$ at 184°C) ($R = 0.831 \text{ kJ}(\text{mol.K})$) When K_p and K_c are compared at 184°C it is found that [AIEEE-2005]

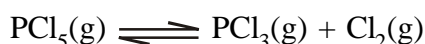
- (1) K_p is less than K_c
(2) K_p is greater than K_c
(3) Whether K_p is greater than, less than or equal to K_c depends upon the total gas pressure
(4) $K_p = K_c$

11. The equilibrium constant for the reaction $\text{SO}_3(g) \rightleftharpoons \text{SO}_2(g) + \frac{1}{2}\text{O}_2(g)$ is $K_c = 4.9 \times 10^{-2}$. The value of K_c for the reaction [AIEEE-2006]



- (1) 2.40×10^{-3} (2) 9.8×10^{-2} (3) 4.9×10^{-2} (4) 416

12. Phosphorus pentachloride dissociates as follows, in a closed reaction vessel, [AIEEE-2006]



If total pressure at equilibrium of the reaction mixture is P and degree of dissociation of PCl_5 is x , the partial pressure of PCl_3 will be-

- (1) $\left(\frac{2x}{1-x}\right)P$ (2) $\left(\frac{x}{x-1}\right)P$ (3) $\left(\frac{x}{1-x}\right)P$ (4) $\left(\frac{x}{x+1}\right)P$

13. The equilibrium constants K_{p1} and K_{p2} for the reaction $X \rightleftharpoons 2Y$ and $Z \rightleftharpoons P + Q$, respectively are in the ratio of 1 : 9. If the degree of dissociation of X and Z be equal then the ratio of total pressure at these equilibria is [AIEEE-2008]

- (1) 1 : 36 (2) 1 : 1 (3) 1 : 3 (4) 1 : 9

14. A vessel at 1000 K contains CO_2 with a pressure of 0.5 atm. Some of the CO_2 is converted into CO on the addition of graphite. If the total pressure at equilibrium is 0.8 atm, the value of K is :- [AIEEE-2011]

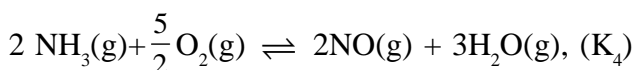
- (1) 0.3 atm (2) 0.18 atm (3) 1.8 atm (4) 3 atm

15. The equilibrium constant (K_C) for the reaction $N_2(g) + O_2(g) \longrightarrow 2NO(g)$ at temperature T is 4×10^{-4} . The value of K_C for the reaction, $NO(g) \longrightarrow \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g)$ at the same temperature is :- [AIEEE-2012]
 (1) 50.0 (2) 0.02 (3) 2.5×10^2 (4) 4×10^{-4}
16. 8 mol of $AB_3(g)$ are introduced into a 1.0 dm^3 vessel. If it dissociates as $2AB_3(g) \rightleftharpoons A_2(g) + 3 B_2(g)$ At equilibrium, 2mol of A_2 are found to be present. The equilibrium constant of this reaction is :- [JEE-MAINS(online)-12]
 (1) 36 (2) 3 (3) 27 (4) 2
17. The value of K_p for the equilibrium reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ is 2. The percentage dissociation of $N_2O_4(g)$ at a pressure of 0.5 atm is [JEE-MAINS(online)-12]
 (1) 71 (2) 50 (3) 88 (4) 25
18. K_1 , K_2 and K_3 are the equilibrium constants of the following reactions (I), (II) and (III), respectively [JEE-MAINS(online)-12]
 (I) $N_2 + 2O_2 \rightleftharpoons 2NO_2$ (II) $2NO_2 \rightleftharpoons N_2 + 2O_2$
 (III) $NO_2 \rightleftharpoons \frac{1}{2}N_2 + O_2$

The correct relation from the following is :

- (1) $K_1 = \sqrt{K_2} = K_3$ (2) $K_1 = \frac{1}{K_2} = \frac{1}{K_3}$ (3) $K_1 = \frac{1}{K_2} = K_3$ (4) $K_1 = \frac{1}{K_2} = \frac{1}{(K_3)^2}$
19. One mole of $O_2(g)$ and two moles of $SO_2(g)$ were heated in a closed vessel of one litre capacity at 1098 K. At equilibrium 1.6 moles of $SO_3(g)$ were found. The equilibrium constant K_C of the reaction would be :- [JEE-MAINS(online)-12]
 (1) 60 (2) 80 (3) 30 (4) 40
20. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, K_1 (1) [JEE-MAINS(online)-13]
 $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$, K_2 (2)
 $H_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons H_2O(g)$, K_3 (3)

The equation for the equilibrium constant of the reaction

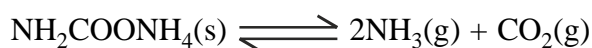


in terms of K_1 , K_2 and K_3 is :

- (1) $\frac{K_1 K_3^2}{K_2}$ (2) $\frac{K_2 K_3^3}{K_1}$ (3) $\frac{K_1 K_2}{K_3}$ (4) $K_1 K_2 K_3$
21. In reaction $A + 2B \rightleftharpoons 2C + D$, initial concentration of B was 1.5 times of $|A|$, but at equilibrium the concentrations of A and B became equal. The equilibrium constant for the reaction is : [JEE-MAINS(online)-13]
 (1) 4 (2) 6 (3) 12 (4) 8

22. For the decomposition of the compound, represented as

[JEE-MAINS(online)-14]



the $K_p = 2.9 \times 10^{-5} \text{ atm}^3$.

If the reaction is started with 1 mol of the compound, the total pressure at equilibrium would be

- (1) $38.8 \times 10^{-2} \text{ atm}$ (2) $1.94 \times 10^{-2} \text{ atm}$
 (3) $5.82 \times 10^{-2} \text{ atm}$ (4) $7.66 \times 10^{-2} \text{ atm}$
23. For the reaction $\text{SO}_{2(\text{g})} + \frac{1}{2}\text{O}_{2(\text{g})} \rightleftharpoons \text{SO}_{3(\text{g})}$, if $K_p = K_c (\text{RT})^x$ where the symbols have usual meaning

then the value of x is : (assuming ideality)

[JEE-MAINS-14]

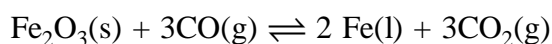
- (1) $\frac{1}{2}$ (2) 1 (3) -1 (4) $-\frac{1}{2}$

24. The equilibrium constants at 298 K for a reaction $\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D}$ is 100. If the initial concentration of all the four species were 1 M each, then equilibrium concentration of D (in mol L^{-1}) will be :

[JEE-MAINS-16]

- (1) 1.182 (2) 0.182 (3) 0.818 (4) 1.818

25. The following reaction occurs in the Blast Furnace where iron ore is reduced to iron metal:



[JEE-MAINS(online)-17]

Using the Le Chatelier's principle, predict which one of the following will **not** disturb the equilibrium?

- (1) Removal of CO_2 (2) Addition of Fe_2O_3 (3) Addition of CO_2 (4) Removal of CO

EXERCISE : J-ADVANCE

- For the reaction $\text{CO}_{(g)} + 2\text{H}_{2(g)} \rightleftharpoons \text{CH}_3\text{OH}_{(g)}$; H_2 is introduced into a five litre flask at 327°C , containing 0.2 mole of $\text{CO}_{(g)}$ and a catalyst till the pressure is 4.92 atmosphere. At this point 0.1 mole of $\text{CH}_3\text{OH}_{(g)}$ is formed. Calculate K_c and K_p . [JEE 1990]
- At temperature T , a compound $\text{AB}_{2(g)}$ dissociates according to the reaction $2\text{AB}_{2(g)} \rightleftharpoons 2\text{AB}_{(g)} + \text{B}_{2(g)}$; with a degree of dissociation 'x', which is small compared to unity. Deduce the expression for 'x' in terms of the equilibrium constant K_p and the total pressure P . [JEE 1994]
- A sample of air consisting of N_2 and O_2 was heated to 2500 K until the equilibrium

$$\text{N}_{2(g)} + \text{O}_{2(g)} \rightleftharpoons 2\text{NO}_{(g)}$$
 was established with an equilibrium constant $K_c = 2.1 \times 10^{-3}$. At equilibrium, the mole% of NO was 1.8. Estimate the initial composition of air in mole fraction of N_2 and O_2 . [JEE 1997]
- The degree of dissociation is 0.4 at 400K & 1.0 atm for the gasoeus reaction $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_{2(g)}$. Assuming ideal behaviour of all gases. Calculate the density of equilibrium mixture at 400K & 1.0 atm pressure. [JEE 1999]
- For the reversible reaction : [JEE 2000]

$$\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$$
 at 500°C . The value of K_p is 1.44×10^{-5} , when partial pressure is measured in atmospheres. The corresponding value of K_c with concentration in mol L^{-1} is :

(A) $1.44 \times 10^{-5} / (0.082 \times 500)^2$ (B) $1.44 \times 10^{-5} / (8.314 \times 773)^2$
 (C) $1.44 \times 10^{-5} / (0.082 \times 500)^2$ (D) $1.44 \times 10^{-5} / (0.082 \times 773)^{-2}$
- When two reactants A and B are mixed to give products C and D, the reaction quotient Q , at the initial stages of the reaction : [JEE 2000]

(A) is zero (B) decrease with time
 (C) independent of time (D) increases with time
- When 3.06g of solid NH_4HS is introduced into a two litre evacuated flask at 27°C , 30% of the solid decomposes into gaseous ammonia and hydrogen sulphide. [JEE 2000]

(i) Calculate K_c & K_p for the reaction at 27°C .
 (ii) What would happen to the equilibrium when more solid NH_4HS is introduced into the flask?
- At constant temperature, the equilibrium constant (K_p) for the decomposition reaction. $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ is expressed by $K_p = 4x^2P/(1-x^2)$ where P is pressure, x is extent of decomposition. Which of the following statement is true ? [JEE 2001]

(A) K_p increases with increase of P (B) K_p increases with increase of x
 (C) K_p increases with decrease of x (D) K_p remains constant with change in P or x

9. Consider the following equilibrium in a closed container : $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$.

At a fixed temperature, the volume of the reaction container is halved. For this change, which of the following statements holds true regarding the equilibrium constant (K_p) and degree of dissociation (α) : [JEE 2002]

- (A) Neither K_p nor α changes
- (B) Both K_p and α change
- (C) K_p changes, but α does not change
- (D) K_p does not change, but α changes

10. The thermal dissociation equilibrium of $\text{CaCO}_3(\text{s})$ is studied under different conditions.



[JEE 2013]

For this equilibrium, the correct statement(s) is(are)

- (A) ΔH is dependent on T
- (B) K is independent of the initial amount of CaCO_3
- (C) K is dependent on the pressure of CO_2 at a given T
- (D) ΔH is independent of the catalyst, if any

ANSWER KEY

EXERCISE # S-I

1. (a) incomplete (b) almost complete

$$2. (a) K_p = \frac{(P_{SO_3})}{(P_{SO_2})(P_{O_2})^{\frac{1}{2}}} ; K_c = \frac{[SO_3]}{[SO_2][O_2]^{\frac{1}{2}}}$$

(b) $K_c = [H_2O]$ [here $H_2O(l)$ is a pure liquid so its concentration is 1.]

$$K_p = P_{H_2O}$$

= vapour pressure

= aqueous tension

(c) $K_c = [NH_3]^2 [CO_2]$ (\because active mass of solid is 1)

$$K_p = (P_{NH_3})^2 P_{CO_2}$$

(d) $K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$ [here H_2O is not in excess]

K_p is not defined for liquid phase.

(e) $K_c = \frac{[NH_4^+][OH^-]}{[NH_3]}$ [here $H_2O(l)$ is in excess (solvent) so its concentration is 1]

(f) $K_{PC} = \frac{P_{H_2} \times [Zn^{2+}]}{[H^+]^2}$ [\because active mass of solid is 1]

3. (a) Here, $\Delta n_g = 1 + 1 - 1 = 1$

$$K_p = K_c (RT)^1 = K_c RT$$

(b) Here, $\Delta n_g = 2 - (3+1) = -2$

$$K_p = K_c (RT)^{-2}$$

(c) Here, $\Delta n_g = 2 - (1+1) = 0$

$$K_p = K_c (RT)^0 = K_c$$

(d) Here, $\Delta n_g = 2 + 1 - 2 = 1$

$$K_p = K_c (RT)^1 = K_c RT$$

(d) Here, $\Delta n_g = 2 - (2 + 1) = -1$

$$K_p = K_c (RT)^{-1} = K_c / RT$$

4. $\therefore K_1 > K_2$

So the stability of $XO < XO_2$

For reactants, stability increases when value of K decreases.

5. $Q_c > K_c$ so the reaction will proceed in the reverse direction.

6. (a) $Q_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$ [\therefore Water is not a solvent here]

(b) $K_c = \frac{(0.171) \times (0.171)}{(1 - 0.171) \times (0.180 - 0.171)} = 3.92$

(c) $Q_c = \frac{(0.214) \times (0.214)}{(0.786) \times (0.286)} = 0.204 \neq K_c$
 \therefore Equilibrium has not been reached.

7. 2×10^9

8. 0.9

9. $K_c = 100$

10. $K_p = 0.2463$

11. 64×10^{-32}

12. $K_c = 0.44$

13. $K_p = 1.2 \text{ atm.}$

14. $[HI] = \frac{1}{3} M$

$[I_2] = [H_2] = \frac{1}{30} M$

15. (a) 0.1 (b) 0.4

16. $[A] = 5 M, [B] = 5 M, [C] = 1 M, [D] = 25 M$

17. new equilibrium	PCl_5	PCl_3	Cl_2
Mole	4	4	2
Partial pressure	20 atm	20 atm	10 atm

18. $\alpha = \sqrt{\frac{K_p}{4P + K_p}}$

19. (A) $\alpha = \frac{4}{5} = 0.8$ (B) $K_c = 16$

20. $K_c = 0.001$

21. $[NO] = 2M, [N_2] = [O_2] = 0.5M$

22. $P_{ClF} = P_{F_2} = 0.1 \text{ atm}, P_{ClF_3} = 0.5 \text{ atm}$ 23. $K_p = 0.4, a \sim 0.1$

24. 50% 25. $K_p = 0.01 \text{ atm}$

26. $K_p = 2.5 \text{ atm}, P = 15 \text{ atm}$ 27. $K = 4$

28. $P_{\text{CS}_2} = 1.8 \text{ atm}$, $P_{\text{S}_2} = 0.2 \text{ atm}$ 29. 22.4 mg
30. $P_{\text{H}_2\text{O}} = 5 \times 10^{-15} \text{ atm}$ 31. 0.821 atm
32. (a) $K = [\text{CH}_3\text{OH}]/[\text{H}_2]^2[\text{CO}]$,
 (b) 1. $[\text{H}_2]$ increase, $[\text{CO}]$ decrease, $[\text{CH}_3\text{OH}]$ increase ; 2. $[\text{H}_2]$ increase, $[\text{CO}]$ decrease, $[\text{CH}_3\text{OH}]$ decrease ; 3. $[\text{H}_2]$ increase, $[\text{CO}]$ increase, $[\text{CH}_3\text{OH}]$ increase ; 4. $[\text{H}_2]$ increase, $[\text{CO}]$ increase, $[\text{CH}_3\text{OH}]$ increase ; 5. $[\text{H}_2]$ increase, $[\text{CO}]$ increase, $[\text{CH}_3\text{OH}]$ decrease ; 6. no change
33. 2
34. 250
35. k_r increase more than k_f , this means that E_a (reverse) is greater than E_a (forward). Hence exothermic reaction.

EXERCISE # S-II

1. Ans.(2.4 atm) 2. Ans.31/27
3. Ans.(0.11) 4. Ans.(2×10^{-4})
5. $[\text{PCl}_3] = [\text{Cl}_2] = \frac{-5 \pm \sqrt{15}}{10} \text{ M}$
6. (a) $6.667 \times 10^{-3} \text{ mol L}^{-1}$;
 (b) $n(\text{N}_2\text{O}_4) = 0.374 \text{ mol}$; $n(\text{NO}_2) = 0.052 \text{ mol}$;
 (c) 10.49 atm (d) 6.44 %
7. (i) 2; (ii) 1.2 mol/L; (iii) 0.1 moles/hr
8. Ans. $K_c=54$, $n_{\text{HI}}=0.9 \text{ mol}$, $n_{\text{I}_2}=0.05 \text{ mol}$, $n_{\text{H}_2} = 0.3 \text{ mol}$
9. Ans. $3.6 \times 10^{-3} \text{ atm}$
10. Ans.(a) 400mm², 900mm² (b) 4: 9, (c) 72.15 mm Hg
11. Ans. (4) 12. Ans. ($\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$)
13. Ans. (10) 14. $K_{p_1} = \frac{1}{20P_0^2}$; $K_{p_2} = \frac{3}{20P_0^2}$
15. (a) 84 ; (b) 0.095 ; (c) 17.35 %

EXERCISE # O-I

- | | | | |
|---------|---------|---------|---------|
| 1. (D) | 2. (C) | 3. (D)] | 4. (B) |
| 5. (C) | 6. (C) | 7. (A) | 8. (C) |
| 9. (A) | 10. (A) | 11. (A) | 12. (C) |
| 13. (C) | 14. (A) | 15. (B) | 16. (B) |
| 17. (A) | 18. (D) | 19. (B) | 20. (D) |
| 21. (C) | 22. (B) | 23. (B) | 24. (A) |
| 25. (C) | 26. (C) | 27. (C) | 28. (B) |
| 29. (C) | 30. (D) | 31. (A) | 32. (A) |
| 33. (C) | 34. (A) | 35. (D) | |

EXERCISE # O-II

- | | | | |
|----------|------------|------------|--------------|
| 1. (B) | 2. (C,D) | 3. (C,D) | 4. (A,B,C,D) |
| 5. (C,D) | 6. (A,C,D) | 7. (A,B,C) | 8. (C,D) |
| 9. (A,C) | 10. (B) | 11. (D) | 12. (A) |
| 13. (A) | 14. (B) | 15. (C) | 16. (B) |
| 17. (A) | 18. (D) | 19. (A) | 20. (A) |

Match the column :

21. (A) - P,R,S (B) - P,Q,R,S (C) - P, Q, R, S ; (D) - Q
 22. A - (s), B - (p,q,s), C - (p,q,r), D - (r)
 23. (D) 24. (C) 25. (A)

EXERCISE # J-MAIN

- | | | | |
|-------------|-------------|-------------|-------------|
| 1. Ans.(3) | 2. Ans.(3) | 3. Ans.(1) | 4. Ans.(1) |
| 5. Ans.(2) | 6. Ans.(1) | 7. Ans.(4) | 8. Ans.(2). |
| 9. Ans.(3) | 10. Ans.(2) | 11. Ans.(4) | 12. Ans.(4) |
| 13. Ans.(1) | 14. Ans.(3) | 15. Ans.(1) | 16. Ans(3) |
| 17. Ans(1) | 18. Ans(4) | 19. Ans(2) | 20. Ans(2) |
| 21. Ans(1) | 22. Ans(3) | 23. Ans.(4) | 24. Ans.(4) |
| 25. Ans.(2) | | | |

EXERCISE # J-ADVANCE

1. $K_c = 279.64 \text{ litre}^2 \text{ mole}^{-2}$; $K_p = 0.115 \text{ atm}^{-2}$
 2. $x = \sqrt[3]{\frac{2K_p}{P}}$ 3. 79%, 21% 4. Ans. 4.54 g dm^{-3}
 5. Ans.(D) 6. Ans.(D)
 7. (i) $K_c = 8.1 \times 10^{-5} \text{ mol}^2 \text{ L}^2$; $K_p = 4.91 \times 10^{-2} \text{ atm}^2$ (ii) No effect;
 8. Ans.(D) 9. Ans.(D) 10. Ans.(A,B,D)

CHEMISTRY IN EVERYDAY LIFE**1. CHEMICALS IN FOOD**

Chemicals are added to food for (i) their preservation, (ii) enhancing their appeal, and (iii) adding nutritive value in them. Main categories of food additives are as follows:

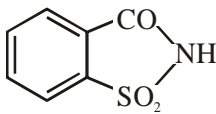
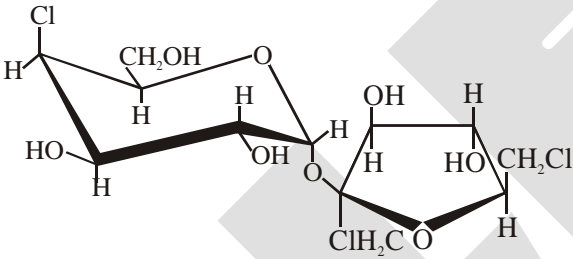
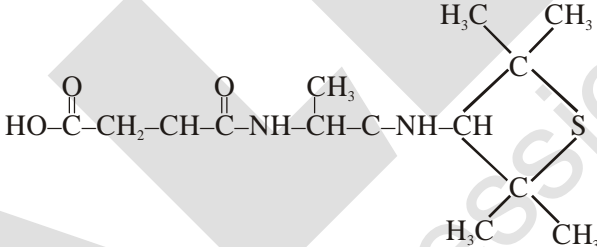
- (i) Food colours
- (ii) Flavours and sweeteners
- (iii) Fat emulsifiers and stabilising agents
- (iv) Flour improvers - antistaling agents and bleaches
- (v) Antioxidants
- (vi) Preservatives
- (vii) Nutritional supplements such as minerals, vitamins and amino acids.

Except for chemicals of category (vii), none of the above additives have nutritive value. These are added either to increase the shelf life of stored food or for cosmetic purposes. In this Section we will discuss only sweeteners and food preservatives.

Artificial Sweetening Agents :

Natural sweeteners, e.g., sucrose add to calorie intake and therefore many people prefer to use artificial sweeteners. Ortho-sulphobenzimide, also called saccharin, is the first popular artificial sweetening agent. It has been used as a sweetening agent ever since it was discovered in 1879. It is about 550 times as sweet as cane sugar. It is excreted from the body in urine unchanged. It appears to be entirely inert and harmless when taken. Its use is of great value to diabetic persons and people who need to control intake of calories. Some other commonly marketed artificial sweeteners are given in Table 16.1.

Table: Artificial Sweeteners

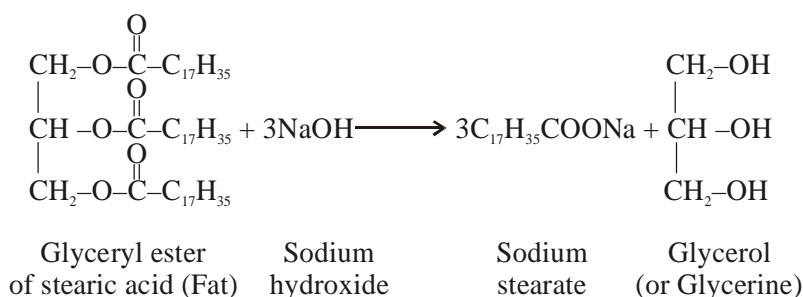
Artificial Sweetner	Artificial Sweetner	Seetness value in Comparisonh to cane sugar
Aspartame	$\text{HO}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\underset{\text{NH}_2}{\text{CH}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}-\underset{\text{CH}_2}{\text{CH}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OCH}_3$ <p>Aspartic acid part</p> <p>Phenylalanine methyl ester part</p>	100
Saccharin		550
Sucralose		600
Alitame		2000

Aspartame is the most successful and widely used artificial sweetener. It is roughly 100 times as sweet as cane sugar. It is methyl ester of dipeptide formed from aspartic acid and phenylalanine. Use of aspartame is limited to cold foods and soft drinks because it is unstable at cooking temperature.

Alitame is high potency sweetener, although it is more stable than aspartame, the control of sweetness of food is difficult while using it.

Sucralose is trichloro derivative of sucrose. Its appearance and taste are like sugar. It is stable at cooking temperature. It does not provide calories.

Soaps :



Soaps are the detergents used since long. Soaps used for cleaning purpose are sodium or potassium salts of long chain fatty acids, e.g., stearic, oleic and palmitic acids. Soaps containing sodium salts are formed by heating fat (i.e., glyceryl ester of fatty acid) with aqueous sodium hydroxide solution. This reaction is known as saponification.

In this reaction, esters of fatty acids are hydrolysed and the soap obtained remains in colloidal form. It is precipitated from the solution by adding sodium chloride. The solution left after removing the soap contains glycerol, which can be recovered by fractional distillation. Only sodium and potassium soaps are soluble in water and are used for cleaning purposes. Generally potassium soaps are soft to the skin than sodium soaps. These can be prepared by using potassium hydroxide solution in place of sodium hydroxide.

Types of soaps :

Basically all soaps are made by boiling fats or oils with suitable soluble hydroxide. Variations are made by using different raw materials.

Toilet soaps are prepared by using better grades of fats and oils and care is taken to remove excess alkali. Colour and perfumes are added to make these more attractive.

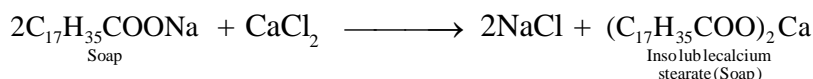
Soaps that float in water are made by beating tiny air bubbles before their hardening. Transparent soaps are made by dissolving the soap in ethanol and then evaporating the excess solvent.

In medicated soaps, substances of medicinal value are added. In some soaps, deodorants are added. Shaving soaps contain glycerol to prevent rapid drying. A gum called, rosin is added while making them. It forms sodium rosinate which lathers well. Laundry soaps contain fillers like sodium rosinate, sodium silicate, borax and sodium carbonate.

Soap chips are made by running a thin sheet of melted soap onto a cool cylinder and scraping off the soaps in small broken pieces. Soap granules are dried miniature soap bubbles. Soap powders and scouring soaps contain some soap, a scouring agent (abrasive) such as powdered pumice or finely divided sand, and builders like sodium carbonate and trisodium phosphate. Builders make the soaps act more rapidly. The cleansing action of soap has been discussed in Unit 5.

Why do soaps not work in hard water ?

Hard water contains calcium and magnesium ions. These ions form insoluble calcium and magnesium soaps respectively when sodium or potassium soaps are dissolved in hard water.



These insoluble soaps separate as scum in water and are useless as cleansing agent. In fact these are hinderance to good washing, because the precipitate adheres onto the fibre of the cloth as gummy mass. Hair washed with hard water looks dull because of this sticky precipitate. Dye does not absorb evenly on cloth washed with soap using hard water, because of this gummy mass.

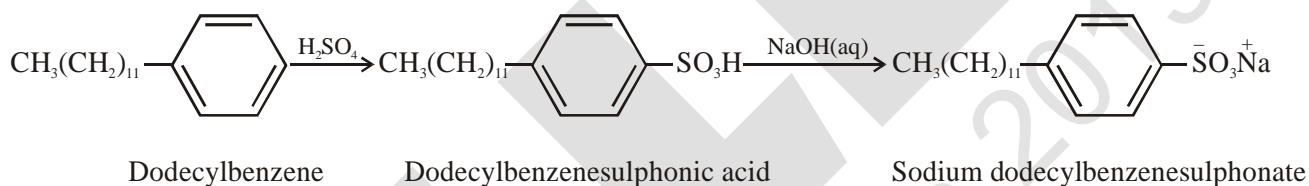
Synthetic Detergents :

Synthetic detergents are cleansing agents which have all the properties of soaps, but which actually do not contain any soap. These can be used both in soft and hard water as they give foam even in hard water. Some of the detergents give foam even in ice cold water.

Synthetic detergents are mainly classified into three categories:

- (i) Anionic detergents (ii) Cationic detergents and (iii) Non-ionic detergents

- (i) **Anionic Detergents:** Anionic detergents are sodium salts of sulphonated long chain alcohols or hydrocarbons. Alkyl hydrogensulphates formed by treating long chain alcohols with concentrated sulphuric acid are neutralised with alkali to form anionic detergents. Similarly alkyl benzene sulphonates are obtained by neutralising alkyl benzene sulphonic acids with alkali.

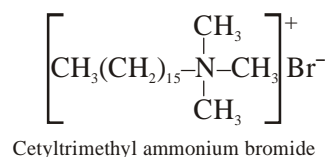


In anionic detergents, the anionic part of the molecule is involved in the cleansing action. Sodium salts of alkylbenzenesulphonates are an important class of anionic detergents.

They are mostly used for household work. Anionic detergents are also used in toothpastes.

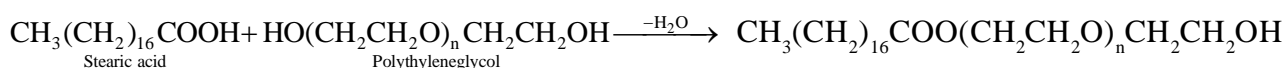
- (ii) **Cationic Detergents:** Cationic detergents are quaternary ammonium salts of amines with acetates, chlorides or bromides

as anions. Cationic part possess a long hydrocarbon chain and a positive charge on nitrogen atom. Hence, these are called cationic detergents. Cetyltrimethylammonium bromide is a popular cationic detergent and is used in hair conditioners.



Cationic detergents have germicidal properties and are expensive, therefore, these are of limited use.

- (iii) **Non-ionic Detergents:** Non-ionic detergents do not contain any ion in their constitution. One such detergent is formed when stearic acid reacts with polyethyleneglycol.



Liquid dishwashing detergents are non-ionic type. Mechanism of cleansing action of this type of detergents is the same as that of soaps. These also remove grease and oil by micelle formation. Main problem that appears in the use of detergents is that if their hydrocarbon chain is highly branched, then bacteria cannot degrade this easily. Slow degradation of detergents leads to their accumulation. Effluents containing such detergents reach the rivers, ponds, etc.

These persist in water even after sewage treatment and cause foaming in rivers, ponds and streams and their water gets polluted.

These days the branching of the hydrocarbon chain is controlled and kept to the minimum. Unbranched chains can be biodegraded more easily and hence pollution is prevented.

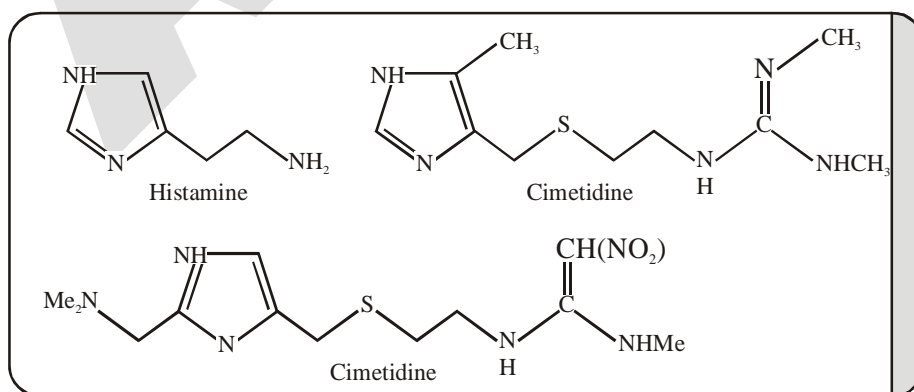
Therapeutic Action of Different Classes of Drugs :

In this Section, we shall discuss the therapeutic action of a few important classes of drugs.

Antacids :

Over production of acid in the stomach causes irritation and pain. In severe cases, ulcers are developed in the stomach. Until 1970, only treatment for acidity was administration of antacids, such as sodium hydrogencarbonate or a mixture of aluminium and magnesium hydroxide. However, excessive hydrogencarbonate can make the stomach alkaline and trigger the production of even more acid. Metal hydroxides are better alternatives because of being insoluble, these do not increase the pH above neutrality. These treatments control only symptoms, and not the cause. Therefore, with these metal salts, the patients cannot be treated easily. In advanced stages, ulcers become life threatening and its only treatment is removal of the affected part of the stomach.

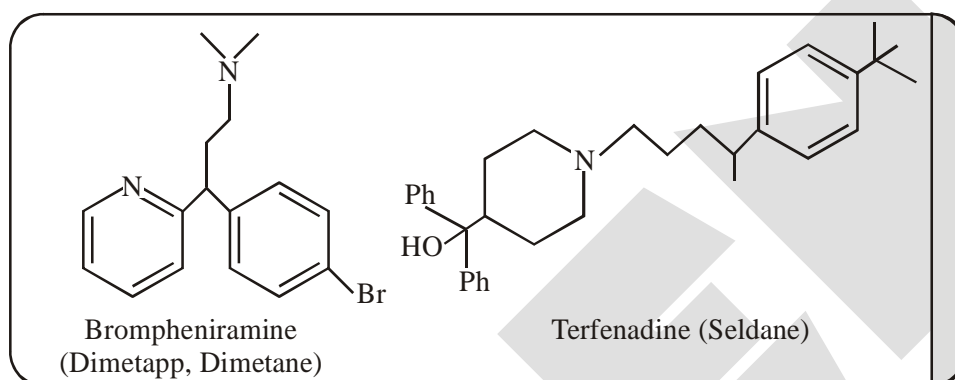
A major breakthrough in the treatment of hyperacidity came through the discovery according to which a chemical, histamine, stimulates the secretion of pepsin and hydrochloric acid in the stomach. The drug cimetidine (Tegamet), was designed to prevent the interaction of histamine with the receptors present in the stomach wall. This resulted in release of lesser amount of acid. The importance of the drug was so much that it remained the largest selling drug in the world until another drug, ranitidine (Zantac), was discovered.



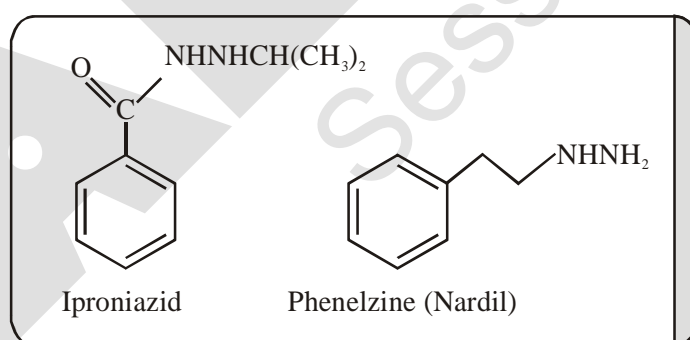
Antihistamine :

Histamine is a potent vasodilator. It has various functions. It contracts the smooth muscles in the bronchi and gut and relaxes other muscles, such as those in the walls of fine blood vessels. Histamine is also responsible for the nasal congestion associated with common cold and allergic response to pollen. Synthetic drugs, brompheniramine (Dimetapp) and terfenadine (Seldane), act as antihistamines. They interfere with the natural action of histamine by competing with histamine for binding sites of receptor where histamine exerts its effect.

Now the question that arises is, "Why do above mentioned antihistamines not affect the secretion of acid in stomach?" The reason is that antiallergic and antacid drugs work on different receptors.

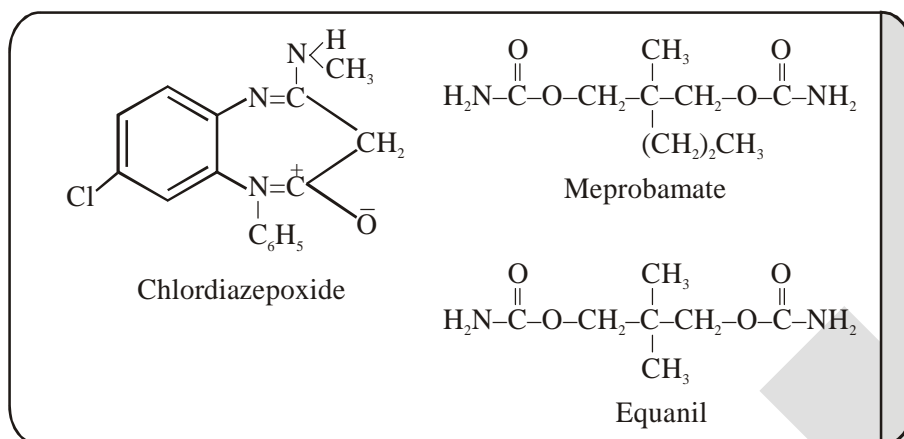
**Neurologically Active Drugs****(a) Tranquilizers**

Tranquilizers and analgesics are neurologically active drugs. These affect the message transfer mechanism from nerve to receptor. Tranquilizers are a class of chemical compounds used for the treatment of stress, and mild or even severe mental diseases. These relieve anxiety, stress, irritability or excitement by inducing a sense of well-being. They form an essential component of sleeping pills. There are various types of tranquilizers. They function by different mechanisms. For example, noradrenaline is one of the neurotransmitters that plays a role in mood changes.

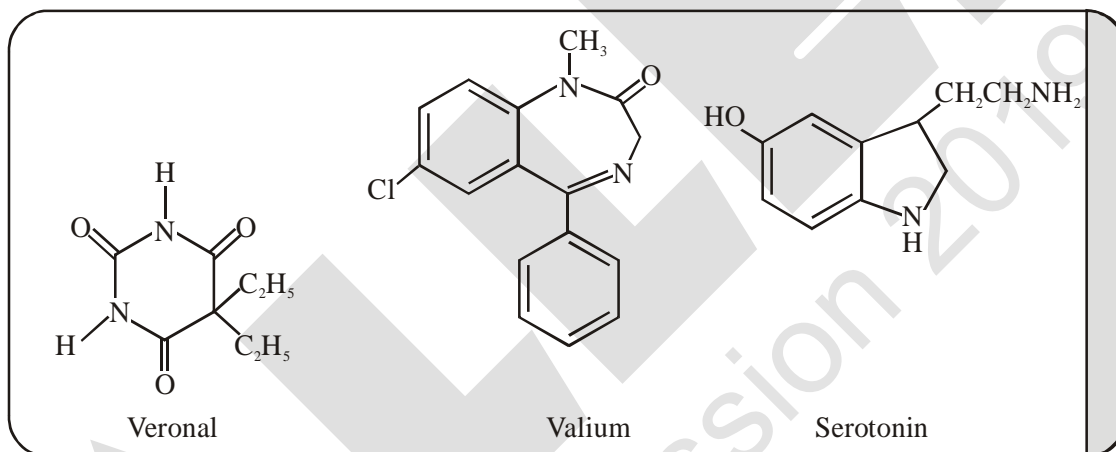


If the level of noradrenaline is low for some reason, then the signal-sending activity becomes low, and the person suffers from depression. In such situations, antidepressant drugs are required. These drugs inhibit the enzymes which catalyse the degradation of noradrenaline. If the enzyme is inhibited, this important neurotransmitter is slowly metabolised and can activate its receptor for longer periods of time, thus counteracting the effect of depression. Iproniazid and phenelzine are two such drugs. Some tranquilizers namely, chlordiazepoxide and meprobamate, are relatively mild tranquilizers suitable for relieving tension.

Equanil is used in controlling depression and hypertension.



Derivatives of barbituric acid viz., veronal, amytal, nembutal, luminal and seconal constitute an important class of tranquilizers. These derivatives are called barbiturates. Barbiturates are hypnotic, i.e., sleep producing agents. Some other substances used as tranquilizers are valium and serotonin.



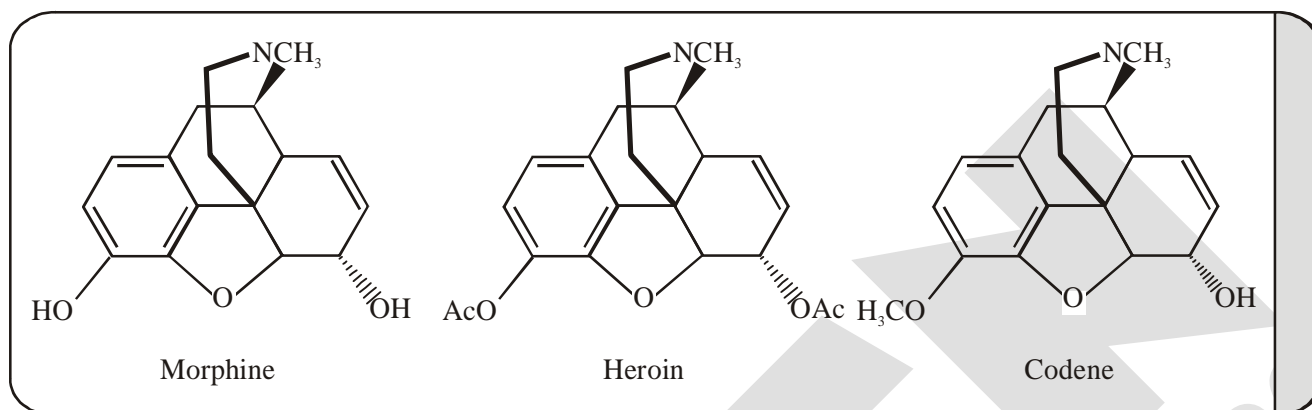
(b) Analgesics

Analgesics reduce or abolish pain without causing impairment of consciousness, mental confusion, incoordination or paralysis or some other disturbances of nervous system. These are classified as follows:

- (i) Non-narcotic (non-addictive) analgesics
- (ii) Narcotic drugs
- (i) **Non-narcotic (non-addictive) analgesics:** Aspirin and paracetamol belong to the class of non-narcotic analgesics. Aspirin is the most familiar example. Aspirin inhibits the synthesis of chemicals known as prostaglandins which stimulate inflammation in the tissue and cause pain. These drugs are effective in relieving skeletal pain such as that due to arthritis. These drugs have many other effects such as reducing fever (antipyretic) and preventing platelet coagulation. Because of its anti blood clotting action, aspirin finds use in prevention of heart attacks.

- (ii) **Narcotic analgesics:** Morphine and many of its homologues, when administered in medicinal doses, relieve pain and produce sleep. In poisonous doses, these produce stupor, coma, convulsions and ultimately death. Morphine narcotics are sometimes referred to as opiates, since they are obtained from the opium poppy.

These analgesics are chiefly used for the relief of postoperative pain, cardiac pain and pains of terminal cancer, and in child birth.



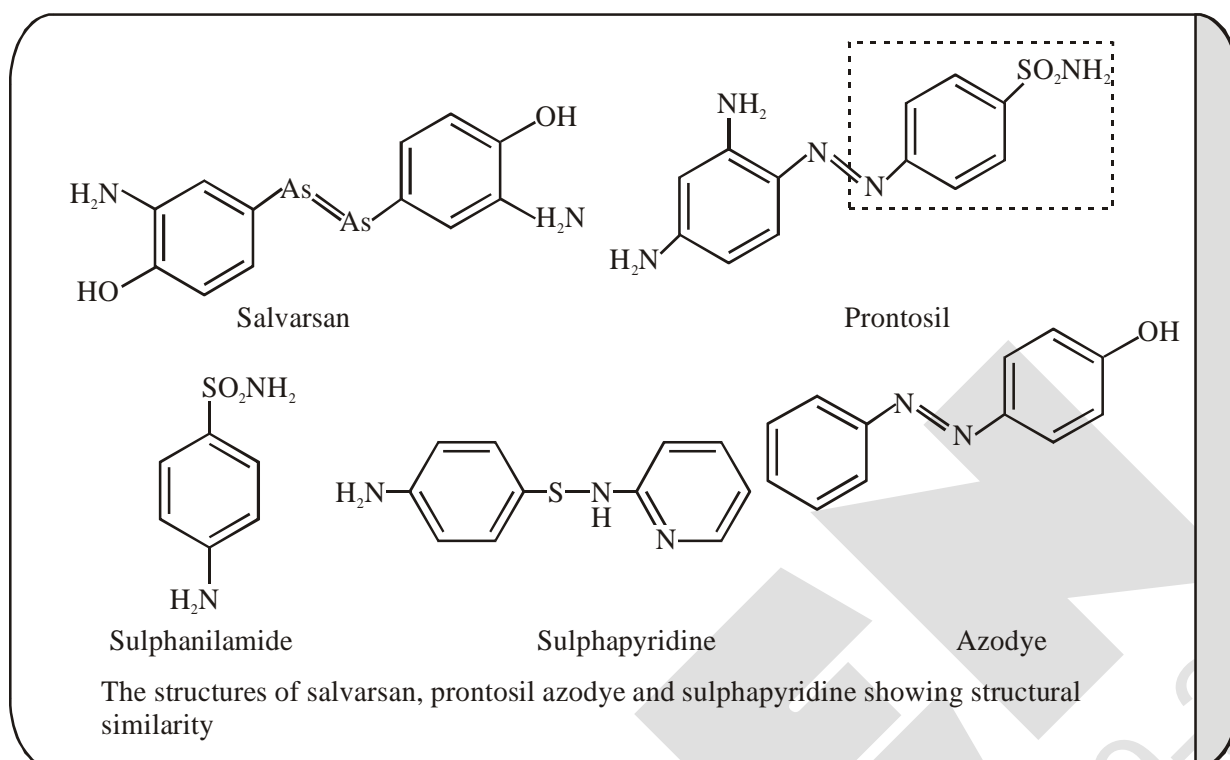
Antimicrobials

Diseases in human beings and animals may be caused by a variety of microorganisms such as bacteria, virus, fungi and other pathogens. An antimicrobial tends to destroy/prevent development or inhibit the pathogenic action of microbes such as bacteria (antibacterial drugs), fungi (antifungal agents), virus (antiviral agents), or other parasites (antiparasitic drugs) selectively. Antibiotics, antiseptics and disinfectants are antimicrobial drugs.

(a) Antibiotics

Antibiotics are used as drugs to treat infections because of their low toxicity for humans and animals. Initially antibiotics were classified as chemical substances produced by microorganisms (bacteria, fungi and molds) that inhibit the growth or even destroy microorganisms. The development of synthetic methods has helped in synthesising some of the compounds that were originally discovered as products of microorganisms. Also, some purely synthetic compounds have antibacterial activity, and therefore, definition of antibiotic has been modified. An antibiotic now refers to a substance produced wholly or partly by chemical synthesis, which in low concentrations inhibits the growth or destroys microorganisms by intervening in their metabolic processes.

The search for chemicals that would adversely affect invading bacteria but not the host began in the nineteenth century. Paul Ehrlich, a German bacteriologist, conceived this idea. He investigated arsenic based structures in order to produce less toxic substances for the treatment of syphilis. He developed the medicine, arsphenamine, known as salvarsan. Paul Ehrlich got Nobel prize for Medicine in 1908 for this discovery. It was the first effective treatment discovered for syphilis. Although salvarsan is toxic to human beings, its effect on the bacteria, spirochete, which causes syphilis is much greater than on human beings. At the same time, Ehrlich was working on azodyes also. He noted that there is similarity in structures of salvarsan and



azodyes. The $-\text{As} = \text{As}-$ linkage present in arsphenamine resembles the $-\text{N} = \text{N}-$ linkage present in azodyes in the sense that arsenic atom is present in place of nitrogen. He also noted tissues getting coloured by dyes selectively. Therefore, Ehrlich began to search for the compounds which resemble in structure to azodyes and selectively bind to bacteria. In 1932, he succeeded in preparing the first effective antibacterial agent, prontosil, which resembles in structure to the compound, salvarsan. Soon it was discovered that in the body prontosil is converted to a compound called sulphanilamide, which is the real active compound. Thus the sulpha drugs were discovered. A large range of sulphonamide analogues was synthesised. One of the most effective is sulphapyridine.

H.W. Florey and Alexander Fleming shared the Noble prize for Medicine in 1945 for their independent contributions to the development of penicillin

Despite the success of sulfonamides, the real revolution in antibacterial therapy began with the discovery of Alexander Fleming in 1929, of the antibacterial properties of a *Penicillium* fungus. Isolation and purification of active compound to accumulate sufficient material for clinical trials took thirteen years. Antibiotics have either cidal (killing) effect or a static (inhibitory) effect on microbes. A few examples of the two types of antibiotics are as follows:

Bactericidal

Penicillin
Aminoglycosides
Ofloxacin

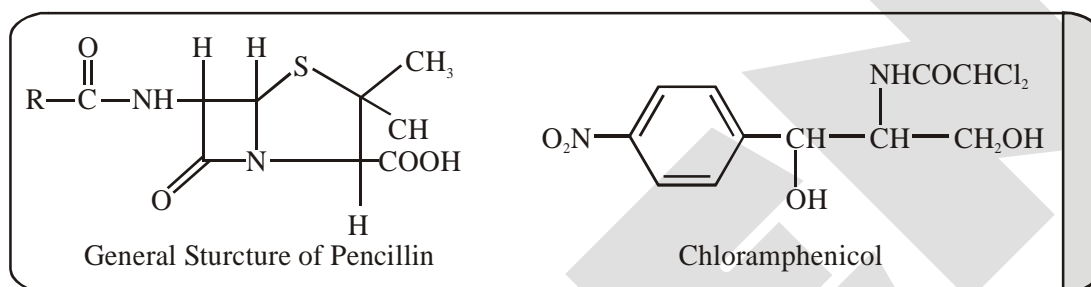
Bacteriostatic

Erythromycin
Tetracycline
Chloramphenicol

The range of bacteria or other microorganisms that are affected by a certain antibiotic is expressed as its spectrum of action. Antibiotics which kill or inhibit a wide range of Gram-positive and Gram-negative bacteria are said to be broad spectrum antibiotics.

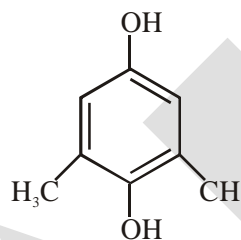
Those effective mainly against Gram-positive or Gram-negative bacteria are narrow spectrum antibiotics. If effective against a single organism or disease, they are referred to as limited spectrum antibiotics. Penicillin G has a narrow spectrum. Ampicillin and Amoxycillin are synthetic modifications of penicillins. These have broad spectrum. It is absolutely essential to test the patients for sensitivity (allergy) to penicillin before it is administered. In India, penicillin is manufactured at the Hindustan Antibiotics in Pimpri and in private sector industry.

Chloramphenicol, isolated in 1947, is a broad spectrum antibiotic. It is rapidly absorbed from the gastrointestinal tract and hence can be given orally in case of typhoid, dysentery, acute fever, certain form of urinary infections, meningitis and pneumonia. Vancomycin and ofloxacin are the other important broad spectrum antibiotics. The antibiotic dysidazirine is supposed to be toxic towards certain strains of cancer cells.

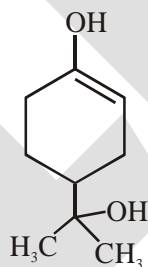


(b) Antiseptics and disinfectants

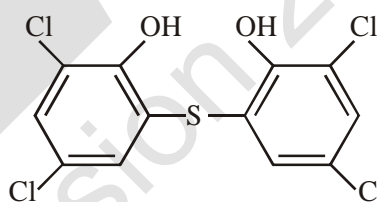
Antiseptics and disinfectants are also the chemicals which either kill or prevent the growth of microorganisms.



Chloroxylenol



Terpineol



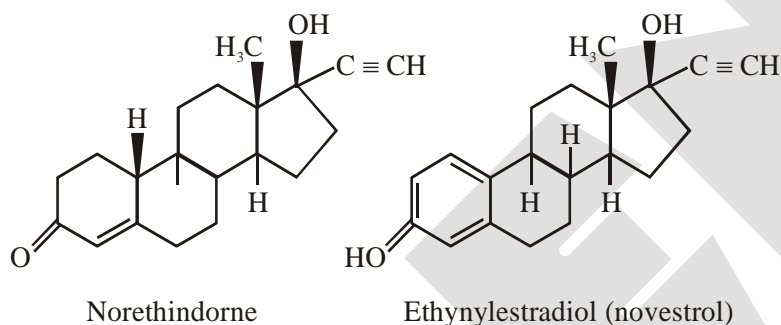
Bithionol

Antiseptics are applied to the living tissues such as wounds, cuts, ulcers and diseased skin surfaces. Examples are furacine, soframycin, etc. These are not ingested like antibiotics. Commonly used antiseptic, dettol is a mixture of chloroxylenol and terpineol. Bithionol (the compound is also called bithional) is added to soaps to impart antiseptic properties. Iodine is a powerful antiseptic. Its 2-3 per cent solution in alcoholwater mixture is known as tincture of iodine. It is applied on wounds. Iodoform is also used as an antiseptic for wounds. Boric acid in dilute aqueous solution is weak antiseptic for eyes.

Disinfectants are applied to inanimate objects such as floors, drainage system, instruments, etc. Same substances can act as an antiseptic as well as disinfectant by varying the concentration. For example, 0.2 per cent solution of phenol is an antiseptic while its one percent solution is disinfectant. Chlorine in the concentration of 0.2 to 0.4 ppm in aqueous solution and sulphur dioxide in very low concentrations, are disinfectants.

Antifertility Drugs

Antibiotic revolution has provided long and healthy life to people. The life expectancy has almost doubled. The increased population has caused many social problems in terms of food resources, environmental issues, employment, etc. To control these problems, population is required to be controlled. This has led to the concept of family planning. Antifertility drugs are of use in this direction. Birth control pills essentially contain a mixture of synthetic estrogen and progesterone derivatives. Both of these compounds are hormones. It is known that progesterone suppresses ovulation. Synthetic progesterone derivatives are more potent than progesterone. Norethindrone is an example of synthetic progesterone derivative most widely used as antifertility drug. The estrogen derivative which is used in combination with progesterone derivative is ethynylestradiol (novestrol).



SUMMARY

Medicine or Drugs

Chemical substances helping to a human body or an animal either for treatment of diseases or to reduce suffering from pain are called medicine or drug.

The treatment of disease by chemical compound which destroy the micro organism without attacking the tissue of the human body is known as chemotherapy, and the compounds used are called chemotherapeutic agent.

Various type of medicinal compounds are -

(A) Antiseptics :

Which prevent or destroy the growth of the harmful micro organism, common antiseptics are- Dettol, Savlon, Cetavelon, acriflavin, Iodine, methylene blue, mercurochrome & KMnO_4 .

Dettol is a mixture of chloroxylenol and terpineol. Its dilute solution is used to clean wounds.

Bithional -It is added to soap to impart antiseptic properties

(B) Disinfectants :

The chemical compounds capable of completely destroying the micro organism are termed as disinfectants. These are toxic to living tissues.

These are utilized for sterilization of floor, toilets instruments & cloths.

eg. 1% solution of phenol in disinfectant while 0.2% solution of phenol is antiseptic.

(C) Analgesics :

The substance which are used to get relief from pain. These are of two types -

- (a) Narcotics or habit forming drugs
- (b) Non-narcotics

(a) Narcotics : These are alkaloids and mostly opium products, causes sleep and unconsciousness when taken in higher doses.

e.g. Morphine, codeine, heroine

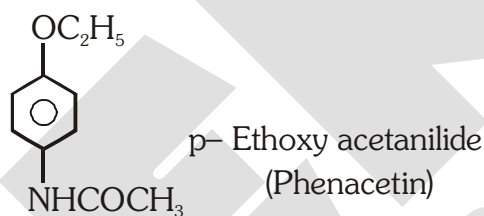
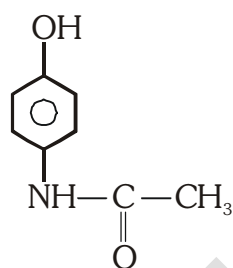
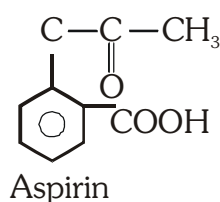
(b) Non-narcotics : Analgesics belonging to this category are effective antipyretics also.

e.g. Aspirin & novalgin, Ibuprofen, Naproxen

(D) Antipyretics :

To bring down the body temp. in high fever are called antipyretics.

e.g : (a) Aspirin, (b) Analgin (Novalgin), (c) Paracetamol, (d) Phenacetin

**(E) Antimalarials :**

To bring down the body temperature during malarial fever.

e.g. Quinine, Chloroquine, Paraquine and Primaquine etc.

(F) Tranquilizers :

The chemical substances which acts on the central nervous system and has a calming effect. Since these are used for mental diseases so are known as psychotherapeutic drugs.

They are of two types - (a) Sedative or hypnotics (b) Mood elevators

(a) **Sedative** : Reduce nervous tension and promote relaxation. e.g. Reserpine, barbituric acid and its

derivatives as luminal & seconal.

- (b) **Mood elevators or Antidepressants** : A drug used for treatment of highly depressed patient, who has lost his confidence.

Example : Benzedrine (amphetamine)

(G) Anaesthetics :

These are chemical substances helping for producing general or local insensibility to pain and other sensation.

These are of two types (a) General (b) Local

- (a) **General** : - Produce unconsciousness and are given at the time of major surgical operations.

Example : Gaseous form → Nitrous oxide, ethylene, cyclopropane etc.

Liquid form → Chloroform, divinyl ether and sodium pentothal etc.

- (b) **Local anaesthetics:** Produce loss of sensation on a small portion of the body. It is used for minor operations.

Example : Jelly form → Oxylocain

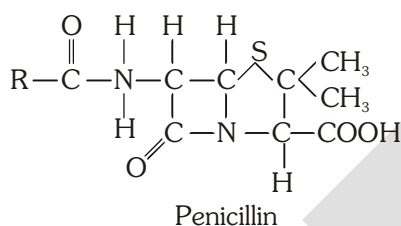
Spray form → Ethyl chloride

Injection form → Procain

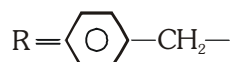
- (H) **Antibiotics :** The chemical substances produced from some micro organism (fungi bacteria or mold) and are used to inhibits the growth of other micro organism.

These are effective in the treatment of infections diseases.

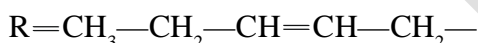
Example : Penicillin - It is highly effective drug for pneumonia, Bronchitis, abcesses, sore throat etc. For other naturally occuring penicillin -



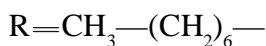
R - May be -



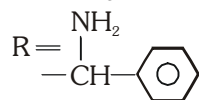
(Penicillin G)



(Penicillin-F)



(Penicillin-K)



(Ampicillin)

Synthetic antibiotics are Streptomycin - (Tuberculosis),

Chloromycetin - (Typhoid, Meningitis, Pneumonia, diarrhoea, dysentary etc.)

Tetracyclins - (Acute fever, trachoma, dysentery & urinary tract infection)

- (I) **Sulpha drugs :** Having great antibacterial powers. These are a group of drugs which are derivatives of sulphanilamide.

Other sulpha drugs are - (a) **Sulphathiazole** -Mainly used in severe infections.

(b) **Sulpha guanidine** - Used in bacillary dysentery

(c) **Sulpha pyridine** - Used in pneumoina

(d) **Sulpha diazine** - Used in dysentery, urinary infection and respiratory infection.

EXERCISE

- An antipyretic is –
(A) Quinine (B) Paracetamol (C) Luminal (D) Piperazine
- Medicine which is an antibiotic is –
(A) Ampicillin (B) Aspirin (C) Chloroquine (D) None of these
- Paracetamol is a/an –
(A) Both antipyretic and analgesic (B) Analgesic
(C) Antipyretic (D) Antimalarial
- Sulpha drugs are derivatives of –
(A) Benzene sulphonic acid (B) Sulphanillic acid
(C) Sulphanilamide (D) p - aminobenzoic acid
- Aspirin is called –
(A) Pyretic (B) Antiseptic (C) Antibiotic (D) Antipyretic
- Which of the following is an antidiabetic drug –
(A) Insulin (B) Penicillin (C) Chloroquine (D) Aspirin
- 2-Acetoxybenzoic acid is called –
(A) Antiseptic (B) Aspirin (C) Antibiotic (D) Mordant dye
- Match List-I with List-II and select the correct answer using the codes given below the lists –

List I	List II
I. Iodoform	A. Anaesthetic
II. Methyl salicylate	B. Antiseptic
III. Diethyl ether	C. Insecticide
IV. Hexachlorocyclohexane	D. Detergent
	E. Pain Balm
(A) I-B, II-E, III-C, IV-D	(B) I-D, II-B, III-A, IV-C
(C) I-B, II-E, III-A, IV-C	(D) I-C, II-A, III-D IV-B
- Arsenic drugs are mainly used in the treatment of–
(A) Jaundice (B) Typhoid (C) Syphilis (D) Cholera
- Aspirin is an acetylation product of –
(A) p-dihydroxybenzene (B) o-hydroxybenzoic acid
(C) o-dihydroxy benzene (D) m-hydroxybenzoic acid
- Chloramphenicol is an –
(A) Analgesic (B) Anaesthetic (C) Antibiotic (D) Antiseptic
- Substances which bring body temperature down are known as –
(A) Antipyretics (B) Analgin (C) Antibiotics (D) Hypnotics
- The drug given during hypertension is –
(A) Streptomycin (B) Chloroxylonol (C) Equanil (D) Aspirin
- Which of the following is known as broad spectrum antibiotic –
(A) Streptomycin (B) Ampicillin (C) Chloramphenicol (D) Penicillin
- Phenol is used as –
(A) An antiseptic (B) A disinfectant (C) Both (A) and (B) (D) None of these

16. The correct match between Item(I) and Item(II) is :

[JEE-MAIN-(Jan)-2019]

Item-I

Item-II

- (A) Nortehindrone (P) Anti-biotic
(B) Ofloxacin (Q) Anti-fertility
(C) Equanil (R) Hypertension
(S) Analgesics

- (A) A-R, B-P, C-S (B) A-Q, B-P, C-R (C) A-R, B-P, C-R (D) A-Q, B-R, C-S

17. The correct match between Item -I and Item-II is :

[JEE-MAIN-(Jan)-2019]

Item – I (drug)		Item – II (test)	
(A)	Chloroxylenol	(P)	Carbylamine Test
(B)	Norethindrone	(Q)	Sodium Hydrogen carbonate Test
(C)	Sulphapyridine	(R)	Ferric chloride test
(D)	Penicillin	(S)	Bayer's test

- (A) A→Q ; B→P ; C→S ; D→R
(B) A→R ; B→P ; C→S ; D→Q
(C) A→R ; B→S ; C→P ; D→Q
(D) A→Q ; B→S ; C→P ; D→R

18. Noradrenaline is a /an

[JEE-MAIN-(April)-2019]

- (A) Neurotransmitter (B) Antidepressant (C) Antihistamine (D) Antacid

ANSWER-KEY

- | | | | |
|------------|------------|------------|------------|
| 1. Ans. B | 2. Ans. A | 3. Ans. A | 4. Ans. C |
| 5. Ans. D | 6. Ans. A | 7. Ans. B | 8. Ans. C |
| 9. Ans. C | 10. Ans. B | 11. Ans. C | 12. Ans. A |
| 13. Ans. C | 14. Ans. C | 15. Ans. C | 16. Ans. B |
| 17. Ans. C | 18. Ans. A | | |

ALLEN
Session 2019-20

NURTURE COURSE
CONCENTRATION TERMS

CONCENTRATION TERMS

1. SOLUTIONS

A solution is a homogenous mixture of two or more pure substances whose composition may be altered within certain limits. Though the solution is homogenous in nature, yet it retains the properties of its constituents.

Generally solution is composed of two components, solute and solvent. Such type of solution is known as binary solutions.

Solvent is that component in solution whose physical state is the same as that of the resulting solution while other component is called as solute. If the physical state of both component is same, than the component in excess is known as solvent and other one is called as solute. Each component in a binary solution can be in any physical state such as liquid, solid and gaseous state.

Table 2.1: Types of Solutions

Type of Solutions	Solute	Solvent	Common Example
Gaseous Solutions	Gas	Gas	Mixture of oxygen and nitrogen gases
	Liquid	Gas	Chloroform mixed with nitrogen gas
	Solid	Gas	Camphor in nitrogen gas
Liquid Solutions	Gas	Liquid	Oxygen dissolved in water
	Liquid	Liquid	Ethanol dissolved in water
	Solid	Liquid	Glucose dissolved in water
Solid Solutions	Gas	Solid	Solution of hydrogen in palladium
	Liquid	Solid	Amalgam of mercury with sodium
	Solid	Solid	Copper dissolved in gold

2. CONCENTRATION TERMS :

The concentration of a solution is the amount of solute dissolved in a known amount of the solvent or solution. Solution can be described as dilute or concentrated solution as per their concentration. A dilute solution has a very small quantity of solute while concentrated solution has a large quantity of solute in solution. Various concentration terms are as follows.

2.1 Mass percentage :

It may be defined as the number of parts of mass of solute per hundred parts by mass of solution.

$$\% \text{ by mass } \left(\frac{w}{W} \right) = \frac{\text{wt. of solute}}{\text{wt. of solution}} \times 100$$

[X % by mass means 100 gm solution contains X gm solute ; \therefore (100 – X) gm solvent]

2.2 Mass-volume percentage (W/V %) :

It may be defined as the mass of solute present in 100 cm³ of solution. For example, If 100 cm³ of solution contains 5 g of sodium hydroxide, then the mass-volume percentage will be 5% solution.

$$\% \left(\frac{w}{V} \right) = \frac{\text{wt. of solute}}{\text{volume of solution}} \times 100 \text{ [for liq. solution]}$$

$$[X \% \left(\frac{w}{V} \right) \text{ means } 100 \text{ ml solution contains } X \text{ gm solute}]$$

2.3 Volume Percent :

It can be represented as % v/v or % volume and used to prepare such solutions in which both components are in liquids state. It is the number of parts of by volume of solute per hundred parts by volume of solution. Therefore,

$$\% \left(\frac{v}{V} \right) = \frac{\text{volume of solute}}{\text{volume of solution}} \times 100$$

$$\mathbf{2.4 \quad \text{Mole \%} = \frac{\text{Moles of solute}}{\text{Total moles}} \times 100}$$

- For gases **% by volume** is same as **mole %**

2.5 Mole Fraction (X) :

Mole fraction may be defined as the ratio of number of moles of one component to the total number of moles of all the components (solute and solvent) present in solution. It is denoted by letter X and the sum of all mole fractions in a solution always equals one.

$$\text{Mole fraction (X)} = \frac{\text{Moles of solute}}{\text{Total moles}}$$

Mole fraction does not depend upon temperature and can be extended to solutions having more than two components.

2.6 Molarity (M) :

Molarity is most common unit for concentration of solution. It is defined as the number of moles of solute present in one litre or one dm³ of the solution or millimol of solute present in one mL of solution.

$$\text{Molarity (M)} = \frac{\text{Mole of solute}}{\text{volume of solution in litre}}$$

- 2.7 Molality (m) :** The number of gram mole of the solute present in 1000 g of the solvent is known as molality of solution. It represented by letter 'm'.

$$\text{Molality (m)} = \frac{\text{Moles of solute}}{\text{Mass of solvent (in kg)}}$$

The unit of molality is mol/kg and it does not effect by temperature.

- 2.8 Parts per million (ppm) :** The very low concentration of solute in solution can be expressed in ppm. It is the numbers of parts by mass of solute per million parts by mass of the solution.

$$\text{Parts per million (ppm)} = \frac{\text{Mass of solute}}{\text{Mass of solvent}} \times 10^6 \cong \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$$

- ◆ Get yourselves very much comfortable in their inter conversion. It is very handy.

Concentration Type	Mathematical Formula	Concept
Percentage by mass	$\% \left(\frac{w}{w} \right) = \frac{\text{Mass of solute} \times 100}{\text{Mass of solution}}$	Mass of solute present in 100 gm of solution.
Volume percentage	$\% \left(\frac{v}{v} \right) = \frac{\text{Volume of solute} \times 100}{\text{Volume of solution}}$	Volume of solute present in 100 cm ³ of solution.
Mass-volume percentage	$\% \left(\frac{w}{v} \right) = \frac{\text{Mass of solute} \times 100}{\text{Volume of solution}}$	Mass of solute present in 100 cm ³ of solution.
Parts per million	$\text{ppm} = \frac{\text{Mass of solute} \times 10^6}{\text{Mass of solution}}$	Parts by mass of solute per million parts by mass of the solution
Mole fraction	$X_A = \frac{\text{Mole of A}}{\text{Mole of A} + \text{Mole of B} + \text{Mole of C} + \dots}$ $X_B = \frac{\text{Mole of B}}{\text{Mole of A} + \text{Mole of B} + \text{Mole of C} + \dots}$	Ratio of number of moles of one component to the total number of moles.
Molarity	$M = \frac{\text{Mole of solute}}{\text{Volume of solution (in L)}}$	Moles of solute in one litre of solution.
Molality	$m = \frac{\text{Mass of solute} \times 1000}{\text{Molar mass of solute} \times \text{Mass of solvent (g)}}$	Moles of solute in one kg of solvent

Ex.1 Calculate the mole fractions of the components of the solution composed by 92 g glycerol and 90 g water ? ($M(\text{water}) = 18$; $M(\text{glycerol}) = 92$)

Ans. Moles of water = $90 \text{ g} / 18 \text{ g} = 5 \text{ mol}$ water
 Moles of glycerol = $92 \text{ g} / 92 \text{ g} = 1 \text{ mol}$ glycerol
 Total moles in solution = $5 + 1 = 6 \text{ mol}$
 Mole fraction of water = $5 \text{ mol} / 6 \text{ mol} = 0.833$
 Mole fraction of glycerol = $1 \text{ mol} / 6 \text{ mol} = 0.167$

Ex.2 What will be the Molarity of solution when water is added to 10 g CaCO_3 to make 100 mL of solution?

Ans. Mol of $\text{CaCO}_3 = 10 / 100 = 0.1$
 Molarity = Mole of solute / Volume of solution (L) = $0.10 \text{ mol} / 0.10 \text{ L}$
 Therefore ; Molarity of given solution = 1.0 M

Ex.3 Calculate the molality of a solution containing 20 g of sodium hydroxide (NaOH) in 250 g of water?

Ans. Moles of sodium hydroxide = $20 / 40 = 0.5 \text{ mol}$ NaOH
 250 gm = 0.25 kg of water
 Hence molality of solution = Mole of solute / Mass of solvent (kg) = $0.5 \text{ mol} / 0.25 \text{ kg}$
 or Molality(m) = 2.0 m

Ex.4 Calculate the grams of copper sulphate (CuSO_4) needed to prepare 250.0 mL of 1.00 M CuSO_4 ?

Ans. Moles of $\text{CuSO}_4 = M \times V = 1 \times \frac{250}{1000}$
 Molar mass of copper sulphate = 159.6 g/mol
 Hence Mass of copper sulphate (gm) = Moles of $\text{CuSO}_4 \times$ Molar mass of copper sulphate.

$$= 1 \times \frac{250}{1000} \times 159.6 \text{ g/mol}$$

$$= 39.9 \text{ gm of Copper sulphate}$$

Ex.5 How many grams of H_2SO_4 are present in 500 ml of 0.2M H_2SO_4 solution ?

Ans. $M = \frac{\text{moles}}{\text{vol.}} \Rightarrow \text{moles of } \text{H}_2\text{SO}_4 = M \times V = 0.2 \times \frac{500}{1000} \text{ L} = 0.1$
 Mass of $\text{H}_2\text{SO}_4 = 0.1 \times 98 = 9.8 \text{ g}$

Ex.6 Calculate the ppm of mercury in water in given sample contain 30 mg of Hg in 500 ml of solution.

Ans. Parts per million = $\frac{\text{Mass of solute} \times 10^6}{\text{Mass of solution}}$

Mass of Hg = 30 mg

Mass of water = $500/1 = 500\text{g} = 50 \times 10^4 \text{ mg}$

(density = mass / volume ; density of water 1 g / ml) $w = \frac{v}{d}$

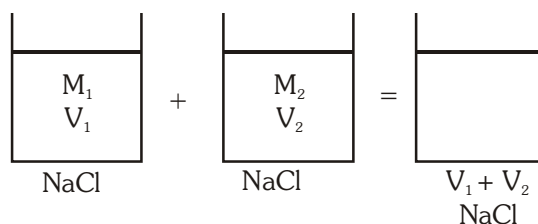
Therefore, ppm of mercury = $\frac{30 \times 10^6}{50 \times 10^4} = 60 \text{ ppm of mercury}$

3. MIXING OF SOLUTIONS :

It is based on law of conservation of moles.

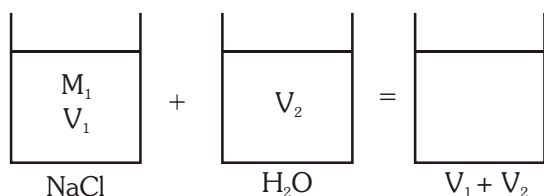
(i) Two solutions having same solute

Final molarity = $\frac{\text{Total moles}}{\text{Total volume}} = \frac{M_1 V_1 + M_2 V_2}{V_1 + V_2}$



(ii) **Dilution Effect :** When a solution is diluted, the moles of solute do not change but molarity changes while on taking out a small volume of solution from a larger volume, the molarity of solution do not change but moles change proportionately.

Final molarity = $\frac{M_1 V_1}{V_1 + V_2}$



n-fold or n-times dilution

\Rightarrow **Final volume = $V_1 + V_2 = n(V_1)$**

Ex.7 50 ml 0.2 M H_2SO_4 is mixed with 50 ml 0.3M H_2SO_4 . Find molarity of final solution.

Ans. $M_f = \frac{\text{Total moles of } \text{H}_2\text{SO}_4}{\text{Total volume}} = \frac{50 \times 0.2 \times 10^{-3} + 50 \times 10^{-3} \times 0.3}{(50 + 50) \times 10^{-3}} = \boxed{0.25 \text{ M}}$

Ex.8 Find final molarity in each case :

Ans. (i) 500 ml 0.1 M HCl + 500 ml 0.2M HCl

$M_f = \frac{500 \times 0.1 + 500 \times 0.2}{500 + 500} = \boxed{0.15 \text{ M}}$

(ii) 50 ml 0.1M HCl + 150 ml 0.3MHCl + 300 ml H_2O

$M_f = \frac{50 \times 0.1 + 150 \times 0.3}{50 + 150 + 300} = \frac{50}{500} = 0.1 \text{ M}$



$$M_f = \frac{\frac{4.9}{98} + \frac{250}{1000} \times 0.1}{\left(\frac{250 + 250}{1000}\right)} = \frac{50 + 25}{500} = \boxed{0.15 \text{ M}}$$

Ex.9 How much water should be added to 2M HCl solution to form 1 litre of 0.5 M HCl ?

Ans. Let V be initial volume

Then mol of HCl = constant

$$2 \times V = 1 \times 0.5 \Rightarrow V = 0.25 \text{ L}$$

$$\text{Volume of water added} = 1 - 0.25 = 0.75 \text{ L}$$

Ex.10 Find number of Na^+ & PO_4^{3-} ions in 250 ml of 0.2M Na_3PO_4 solution.

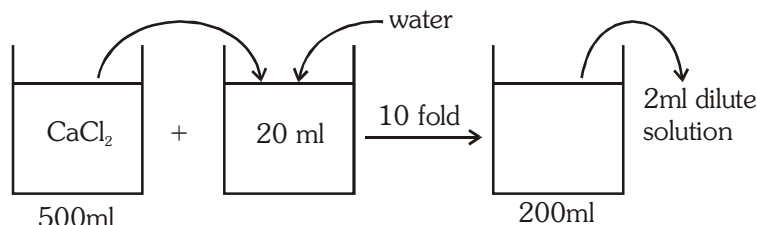
Ans. $\text{Na}_3\text{PO}_4 + \text{aq.} \longrightarrow 3\text{Na}^+(\text{aq}) + \text{PO}_4^{3-}(\text{aq})$ [Ionic compound when added to water ionize completely].

50 millimoles (m.m.) 150 mm 50 mm

$$\text{No. of } \text{Na}^+ \text{ ions} = 150 \times 10^{-3} \times N_A ; \text{No. of } \text{PO}_4^{3-} \text{ ions} = 50 \times 10^{-3} \times N_A$$

Ex.11 1.11g CaCl_2 is added to water forming 500 ml of solution. 20 ml of this solution is taken and diluted 10 folds. Find moles of Cl^- ions in 2 ml of diluted solution.

Ans. $\frac{1.11}{111} = 0.01 \text{ mol CaCl}_2$



$$\text{Moles of CaCl}_2 \text{ in 20ml solution} = \frac{0.01}{500} \times 20 = \frac{0.01}{25}$$

$$\text{In 200 ml solution moles of CaCl}_2 = \frac{0.01}{25} \quad [\text{Note : Dilution does not change moles of solute}]$$

$$\text{In 2 ml of dilute solution moles of CaCl}_2 = \frac{\frac{0.01}{25}}{200} \times 2 = \frac{0.01}{2500} = 8 \times 10^{-6}$$

$$\therefore \text{moles of } \text{Cl}^- = 2 \times 8 \times 10^{-6} = 1.6 \times 10^{-5}$$

Ex.12 What volumes of 1M & 2M H_2SO_4 solution are required to produce 2L of 1.75M H_2SO_4 solution?

Ans. Let XL be vol. of 1M solution.

$\therefore (2 - X)\text{L}$ is vol. of 2M solution.

$$\text{Moles of H}_2\text{SO}_4 = 2 \times 1.75 = 1(X) + (2 - X)2$$

$$3.5 = 4 - X ; X = 0.5 \text{ L}$$

i.e. 0.5L of 1M & 1.5 L of 2M solution required.

Ex.13 80g NaOH was added to 2L water. Find molality of solution if density of water = 1g/mL

Ans. $m = \frac{\text{moles of NaOH}}{\text{mass of H}_2\text{O}} \times 1000 = \frac{80/40}{2 \times 1000} \times 1000 = \boxed{1 \text{ molal}}$

Ex.14 A 100g NaOH solution has 20g NaOH. Find molality.

Ans. $m = \frac{20/40}{100-20} \times 1000 = \frac{500}{80} = \boxed{6.25 \text{ mol/kg}}$

Ex.15 Find molality of aqueous solution of CH_3COOH whose molarity is 2M and density $d = 1.2 \text{ g/mL}$.

Hint : $m = \frac{M}{d - M M_s} \times 1000$

where d = density in g L^{-1} , M = Molarity, m = molality, M_s = molar mass of solute.

Ans. $m = \frac{2}{1200 - 2 \times 60} \times 1000 = \boxed{1.85 \text{ m}}$

Ex.16 A solution is made by mixing 300 ml 1.5M $\text{Al}_2(\text{SO}_4)_3$ + 300 ml 2M CaSO_4 + 400 ml 3.5M CaCl_2

Find final molarity of (1) SO_4^{2-} , (2) Ca^{2+} , (3) Cl^- . [Assume complete dissociation of these compounds].

Ans. (1) $[\text{SO}_4^{2-}]_f = \frac{\text{Total moles}}{\text{Total volume}} = \frac{300 \times 1.5 \times 10^{-3} \times 3 + 300 \times 2 \times 10^{-3}}{(300 + 300 + 400) \times 10^{-3}} = 1.95 \text{ M}$

(2) $[\text{Ca}^{2+}]_f = \frac{300 \times 2 + 400 \times 3.5}{1000} = 2 \text{ M}$

(3) $[\text{Cl}^-]_f = \frac{400 \times 3.5 \times 2}{1000} = 2.8 \text{ M}$

Ex.17 A solution has 80% $\frac{w}{w}$ NaOH with density 2 g L^{-1} . Find (a) Molarity (b) Molality of solution.

Ans. Let V_{lit} be vol. of solution

Mass of solute = $(d \times V) \times \left(\frac{\% w}{w} \right) = 2 \times V \times \frac{80}{100} = 1.6V$

(a) $M = \frac{1.6V/40}{V} = \boxed{0.04 \text{ M}}$ (b) $m = \frac{1.6V/40}{2V - 1.6V} \times 1000 = \boxed{100 \text{ mol kg}^{-1}}$

Ex.18 4.450 g 100 per cent sulphuric acid was added to 82.20 g water and the density of the solution was found to be 1.029 g/cc at 25°C and 1 atm pressure. Calculate (a) the weight percent, (b) the mole fraction, (c) the mole percent, (d) the molality, (e) the molarity of sulphuric acid in the solution under these conditions.

Ans. Sulphuric acid = 4.450 g, Water = 82.20 g \Rightarrow Wt. of solution = 86.65 g
 \therefore Density of solution = 1.029 g/cc.

$$(a) \quad \text{Weight percent} = \frac{\text{wt. of solute}}{\text{wt. of solution}} \times 100 = \frac{4.450}{86.65} \times 100 = 5.14$$

(b) Mole fraction :

$$\text{Mole of solute} = \frac{\text{wt. of solute}}{\text{mol wt. of solute}} = \frac{4.45}{98} = 0.0454$$

$$\text{Mole of solvent} = \frac{82.20}{18} = 4.566$$

$$\text{Total moles in solution} = 0.0454 + 4.566 = 4.6114$$

$$\text{Mole fraction of solute} = \frac{0.0454}{4.6114} = 0.0098$$

$$(c) \quad \text{Mole percent} = \frac{\text{moles of solute}}{\text{Total moles in solution}} \times 100$$

$$= \text{mole fraction of solute} \times 100 = 0.0098 \times 100 = 0.98$$

$$(d) \quad \text{Molality} = \frac{\text{moles of solute}}{\text{mass of solvent (in gm)}} \times 1000$$

$$= \frac{0.0454 \times 1000}{82.2} = 0.552$$

$$(e) \quad \text{Molarity} = \frac{\text{moles of solute}}{\text{litre of solution}}$$

$$\text{Volume of solution} = \frac{\text{Mass}}{\text{Density}} = \frac{86.65}{1.029} \text{ ml}$$

$$= \frac{86.65}{1.029 \times 1000} \text{ litre}$$

$$\text{Molarity} = \frac{0.0454}{\frac{86.65}{1.029 \times 1000}} = \frac{0.0454 \times 1000 \times 1.029}{86.65} = 0.539$$

Ex.19 A solution of KCl has a density of 1.69 g mL^{-1} and is 67% by weight. Find the density of the solution if it is diluted so that the percentage by weight of KCl in the diluted solution is 30%.

Ans. Let the volume of the KCl solution be 100 mL,

$$\text{Weight of KCl solution} = 100 \times 1.69 = 169 \text{ g}$$

$$100 \text{ g of solution contains} = 67 \text{ g of KCl}$$

$$169 \text{ g of solution} = \frac{67}{100} \times 169 = 113.23 \text{ g}$$

Let x mL of H_2O be added.

$$\text{New volume of solution} = (100 + x) \text{ mL}$$

$$\text{New weight of solution} = (169 + x) \text{ g}$$

$$(\text{Since } x \text{ mL of } \text{H}_2\text{O} = x \text{ g of } \text{H}_2\text{O}, d_{\text{H}_2\text{O}} = 1)$$

$$\text{New percentage of the solution} = 30\%$$

$$\% \text{ by weight} = \frac{\text{weight of solute} \times 100}{\text{weight of solution}}$$

$$30 = \frac{113.23}{(169 + x)} \times 100$$

$$x = 208.43 \text{ mL} = 208.43 \text{ g}$$

$$\text{New density} = \frac{\text{New weight of solution}}{\text{New volume of solution}}$$

$$= \frac{(169 + x)}{(100 + x)}$$

$$\frac{(169 + 208.43)}{(100 + 208.43)} = \frac{377.43}{308.43}$$

$$\therefore d = 1.224$$

4. SOME TYPICAL CONCENTRATION TERMS

4.1 PERCENTAGE LABELLING OF OLEUM :

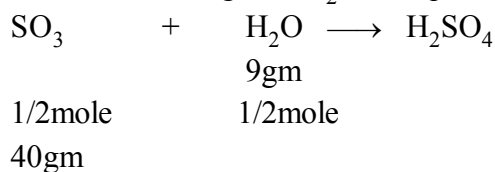
Labelled as '% oleum', it means maximum amount of H_2SO_4 that can be obtained from 100 gm of such oleum (mix of H_2SO_4 and SO_3) by adding sufficient water. For ex. 109 % oleum sample means, with the addition of sufficient water to 100 gm oleum sample 109 gm H_2SO_4 is obtained.

$$\% \text{ labelling of oleum sample} = (100 + x)\%$$

x = mass of H_2O required for the complete conversion of SO_3 in H_2SO_4

Ex.20 Find the mass of free SO_3 present in 100 gm, 109 % oleum sample.

Sol. 109 % means, 9 gm of H_2O is required.

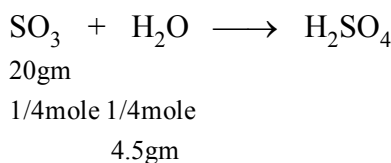


\therefore Mass of free SO_3 = 40 gm, Mass of H_2SO_4 = 60 gm

Note: Work out, what are the maximum and minimum value of the % labelling.

Ex.21 Find the % labelling of 100 gm oleum sample if it contains 20 gm SO_3 .

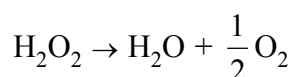
Sol. % labelling of oleum sample = $(100 + x)\%$



\therefore % labelling of oleum sample = $(100 + 4.5)\% = 104.5\%$

II. VOLUME STRENGTH OF H_2O_2 SOLUTION :

Labelled as 'volume H_2O_2 ', it means volume of O_2 (in litre) at STP that can be obtained from 1 litre of such a sample when it decomposes according to



Volume Strength of H_2O_2 Solution = $11.35 \times \text{molarity}$

Ex.22 Find the % w/v of "10 V" H_2O_2 solution-

Sol. Molarity (M) of solution = $\frac{\text{volume strength}}{11.35} = \frac{10}{11.35}$

$$\% \left(\frac{w}{v} \right) = \frac{M \times \text{mol. wt. of solute}}{10} = \frac{10}{11.35} \times \frac{34}{10} = 3\%$$

EXERCISE # S-I

CONCENTRATION TERMS

- Q.1** Calculate the molarity of the following solutions :
- 4g of caustic soda is dissolved in 200 mL of the solution.
 - 5.3 g of anhydrous sodium carbonate is dissolved in 100 mL of solution.
 - 0.365 g of pure HCl gas is dissolved in 50 mL of solution.
- Q.2** Density of a solution containing 13% by mass of sulphuric acid is 0.98 g/mL. Then molarity of solution will be
- Q.3** The density of a solution containing 7.3% by mass of HCl is 1.2 g/mL. Calculate the molarity of the solution.
- Q.4** 15 g of methyl alcohol is present in 100 mL of solution. If density of solution is 0.90 g mL^{-1} . Calculate the mass percentage of methyl alcohol in solution
- Q.5** Units of parts per million (ppm) or per billion (ppb) are often used to describe the concentrations of solutes in very dilute solutions. The units are defined as the number of grams of solute per million or per billion grams of solvent. Bay of Bengal has 2.1 ppm of lithium ions. What is the molality of Li^+ in this water ? ($\text{Li} = 7$)
- Q.6** A 7.0 M solution of KOH in water contains 28% by mass of KOH. What is density of solution in gm/ml ?
- Q.7** The average concentration of Na^+ ion in human body is 3.0 to 3.9 gm per litre. The molarity of Na^+ ion is about.
- Q.8** What is the concentration of chloride ion, in molarity, in a solution containing 10.56 gm $\text{BaCl}_2 \cdot 8\text{H}_2\text{O}$ per litre of solution ? ($\text{Ba} = 137$)
- Q.9** The concentration of a solution is 8% (w/w) and 10% (w/v). Calculate density (in gm/mL) of solution?
- Q.10** The mole fraction of solute in aqueous urea solution is 0.2. Calculate the mass percent of solute ?
- Q.11** The concentration of $\text{Ca}(\text{HCO}_3)_2$ in a sample of hard water is 405 ppm. The density of water sample is 1.0 gm/mL. Calculate the molarity of solution ?
- Q.12** 0.115 gm of sodium metal was dissolved in 500 ml of the solution in distilled water. Calculate the molarity of the solution?
- Q.13** How much BaCl_2 (in gm) would be needed to make 250 ml of a solution having the same concentration of Cl^- as one containing 1.825 gm HCl per 100 ml ? ($\text{Ba} = 137$)
- Q.14** Calculate **molality (m)** of each ion present in the aqueous solution of **2M NH_4Cl** assuming 100% dissociation according to reaction.
- $$\text{NH}_4\text{Cl (aq)} \longrightarrow \text{NH}_4^+ \text{ (aq)} + \text{Cl}^- \text{ (aq)}$$
- Given :** Density of solution = 3.107 gm / ml.
- Q.15** 1200gm aqueous solution contains 200gm calcium bromide (CaBr_2). Calculate molality of solution.

PROBLEMS RELATED WITH MIXING & DILUTION

- Q.16** Find out the volume of 98% w/w H_2SO_4 (density = 1.8 gm/ml), must be diluted to prepare 12.6 litres of 2.0 M sulphuric acid solution.
- Q.17** Determine the volume (in mL) of diluted nitric acid ($d = 1.11 \text{ g mL}^{-1}$, 20% w/v HNO_3) that can be prepared by diluting 50 mL of conc. HNO_3 with water ($d = 1.42 \text{ g mL}^{-1}$, 70% w/v).
- Q.18** 500 ml of 2 M NaCl solution was mixed with 200 ml of 2 M NaCl solution. Calculate the molarity of NaCl in final solution.
- Q.19** Calculate the amount of the water "in mL" which must be added to a given solution of concentration of 40 mg silver nitrate per ml, to yield a solution of concentration of 16 mg silver nitrate per ml?
- Q.20** A mixture containing equimolar amounts of $\text{Ca}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$ requires 0.5 L of 4.0 M HCl to react with it completely. Total moles of the mixture are :
- Q.21** 500 gm of urea solution of mole fraction 0.2 is diluted to 1500 gm. Calculate the mole fraction of solute in the diluted solution?
- Q.22** When V ml of 2.2 M H_2SO_4 solution is mixed with 10 V ml of water, the volume contraction of 2% take place. Calculate the molarity of diluted solution?
- Q.23** What volume (in mL) of 0.8 M AlCl_3 solution should be mixed with 50 ml of 0.2 M CaCl_2 solution to get solution of chloride ion concentration equal to 0.6 M?
- Q.24** A solution containing 200 ml 0.5 M KCl is mixed with 50 ml 19% w/v MgCl_2 and resulting solution is diluted 8 times. Molarity of chloride ion in final solution is :
- Q.25** 100 mL, 3% (w/v) NaOH solution is mixed with 100 ml, 9% (w/v) NaOH solution. The molarity of final solution is-

SOME TYPICAL CONCENTRATION TERMS

- Q.26** An oleum sample is labelled as 118 %, Calculate
- Mass of H_2SO_4 in 100 gm oleum sample.
 - Maximum mass of H_2SO_4 that can be obtained if 30 gm sample is taken.
 - Composition of mixture (mass of components) if 40 gm water is added to 30 gm given oleum sample.
- Q.27** A mixture is prepared by mixing 10 gm H_2SO_4 and 40 gm SO_3 calculate,
- mole fraction of H_2SO_4
 - % labelling of oleum
- Q.28** 500 ml of a H_2O_2 solution on complete decomposition produces 2 moles of H_2O . Calculate the volume strength of H_2O_2 solution?
- Q.29** $2\text{H}_2\text{O}_2(\text{aq}) \longrightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$
- Under conditions where 1 mole of gas occupies 24 dm^3 , X L of $\frac{1}{24}$ M solution of H_2O_2 produces 3 dm^3 of O_2 . Thus X is :-
- Q.30** The volume strength of 100 ml H_2O_2 solution which produce 5.6 litre of oxygen gas at 1 bar & 0°C .

EXERCISE # S-II

- Q.1** What volume of 0.2 M NaOH (in ml) solution should be mixed to 500 ml of 0.5 M NaOH solution so that 300 ml of final solution is completely neutralised by 20 ml of 2 M H_3PO_4 solution.
[Assuming 100% dissociation]
- Q.2** How much minimum volume (in ml) of $\left(\frac{5}{51}\right)$ M aluminium sulphate solution should be added to excess calcium nitrate to obtain at least 1 gm of each salt in the reaction.

$$\text{Al}_2(\text{SO}_4)_3 + 3\text{Ca}(\text{NO}_3)_2 \longrightarrow 2\text{Al}(\text{NO}_3)_3 + 3\text{CaSO}_4$$
- Q.3** One litre of milk weighs 1.035 kg. The butter fat is 4% (v/v) of milk and has density of 875 kg/m^3 . If the density of fat free skimmed milk is 'x' kg/m^3 , the value of (4.8x) is ?
- Q.4** 100 ml of 0.1 M solution of AB (d = 1.5 gm/ml) is mixed with 100 ml of 0.2 M solution of CB_2 (d = 2.5 gm/ml). Calculate the molarity of B^- in final solution if the density of final solution is 4 gm/ml. Assuming AB and CB_2 are non reacting & dissociates completely into A^+ , B^- , C^{+2} .
- Q.5** 60 ml of a "x" % w/w alcohol by weight (d = 0.6 g/cm^3) must be used to prepare 200 cm^3 of 12% alcohol by weight (d = 0.90 g/cm^3). Calculate the value of "x"?
- Q.6** If 0.5 M methanol undergo self dissociation like $\text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{O}^- + \text{H}^+$ & if concentration of H^+ is $2.5 \times 10^{-4} \text{ M}$ then calculate % dissociation of methanol.
- Q.7** 1120 gm of 2 'm' urea solution is mixed with 2480 gm of 4 'm' urea solution. Calculate the molality of the resulting solution?
- Q.8** 50 ml of '20V' H_2O_2 is mixed with 200 ml, '10V' H_2O_2 . The volume strength of resulting solution is
- Q.9** 500 ml of 2M CH_3COOH solution is mixed with 600 ml 12% w/v CH_3COOH solution then calculate the final molarity of solution.
- Q.10** 45.4 V H_2O_2 solution (500 ml) when exposed to atmosphere loses 11.2 litre of O_2 at 1 atm, & 273 K. New molarity of H_2O_2 solution. (Assume no change in volume)

EXERCISE # O-I

- Q.1** 125 ml of 8% w/w NaOH solution (sp. gravity 1) is added to 125 ml of 10% w/v HCl solution. The nature of resultant solution would be _____.
(A) Acidic (B) Basic (C) Neutral (D) Can not be predicted
- Q.2** 8 g NaOH is dissolved in one litre of solution, its molarity is :
(A) 0.8 M (B) 0.4 M (C) 0.2 M (D) 0.1 M
- Q.3** If 18 g of glucose is present in 1000 g of solvent, the solution is said to be :
(A) 1 molar (B) 0.1 molar (C) 0.5 molar (D) 0.1 molal
- Q.4** The molarity of pure water is :
(A) 100 M (B) 55.6 M (C) 50 M (D) 18M
- Q.5** Mole fraction of $C_3H_5(OH)_3$ (glycerine) in a solution of 36 g of water and 46 g of glycerine is :
(A) 0.46 (B) 0.36 (C) 0.20 (D) 0.40
- Q.6** A molal solution is one that contains one mole of a solute in
(A) 1000 g of the solvent (B) one litre of the solution
(C) one litre of the solvent (D) 22.4 litres of the solution
- Q.7** The mole fraction of oxygen in a mixture of 7g of nitrogen and 8g of oxygen is :
(A) $\frac{8}{15}$ (B) 0.5 (C) 0.25 (D) 1.0
- Q.8** The molarity of a solution of sodium chloride (mole wt. = 58.5) in water containing 5.85 gm of sodium chloride in 500 ml of solution is :-
(A) 0.25 (B) 2.0 (C) 1.0 (D) 0.2
- Q.9** The molarity of 98% by wt. H_2SO_4 (d = 1.8 g/ml) is
(A) 6 M (B) 18 M (C) 10 M (D) 4 M
- Q.10** Which one of the following modes of expressing concentration of solution is independent of temperature -
(A) Molarity (B) Molality (C) % w/v (D) Grams per litre
- Q.11** For preparing 0.1 M solution of H_2SO_4 in one litre, we need H_2SO_4 :
(A) 0.98 g (B) 4.9 g (C) 49.0 g (D) 9.8 g
- Q.12** 1000 g aqueous solution of $Ca(NO_3)_2$ contains 10 g of calcium nitrate. Concentration of the solution is :
(A) 10 ppm (B) 100 ppm (C) 1000 ppm (D) 10,000 ppm
- Q.13** How much volume of 3.0 M H_2SO_4 is required for the preparation of 1.0 litre of 1.0 M solution?
(A) 300 ml (B) 320 ml (C) 333.3 ml (D) 350.0 ml
- Q.14** Equal weight of NaCl and KCl are dissolved separately in equal volumes of solutions. Molarity of the solutions will be –
(A) Equal (B) Greater for NaCl
(C) Greater for KCl (D) Uncomparable.

- Q.15** How much water should be added to 200 cc of semimolar solution of NaOH to make it exactly decimolar :-
 (A) 1000 cc (B) 400 cc (C) 800 cc (D) 600 cc
- Q.16** 100 ml of 0.3 M HCl solution is mixed with 200 ml of 0.3 M H_2SO_4 solution. What is the molarity of H^+ in resultant solution ?
 (A) 0.9 (B) 0.6 (C) 0.4 (D) 0.5
- Q.17** H_2O_2 solution used for hair bleaching is sold as a solution of approximately 5.0 g H_2O_2 per 100 mL of the solution. The molecular mass of H_2O_2 is 34. The molarity of this solution is approximately:-
 (A) 0.15 M (B) 1.5 M (C) 3.0 M (D) 3.4 M
- Q.18** 171 g of cane sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) is dissolved in 1 litre of water. The molarity of the solution is :
 (A) 2.0 M (B) 1.0 M (C) 0.5 M (D) 0.25 M
- Q.19** How much grams of CH_3OH should be dissolved in water for preparing 150 ml of 2.0 M CH_3OH solution ?
 (A) 9.6 (B) 2.4 (C) 9.6×10^3 (D) 4.3×10^2
- Q.20** Molality of 20% (w/w) aq. glucose solution is :
 (A) $\frac{25}{18}$ m (B) $\frac{10}{9}$ m (C) $\frac{25}{9}$ m (D) $\frac{5}{18}$ m
- Q.21** Molarity of liquid HCl, if density is 1.17 g/cc. :
 (A) 36.5 M (B) 18.25 M (C) 32.05 M (D) 42.10 M
- Q.22** The molarity of a solution made by mixing 50 ml of conc. H_2SO_4 (18 M) with 50 ml of water, is:
 (A) 36 M (B) 18 M (C) 9 M (D) 6M
- Q.23** Equal volumes of 10% (w/v) of HCl is mixed with 10% (w/v) NaOH solution. The resultant solution be.
 (A) basic (B) neutral
 (C) acidic (D) can't be predicted.
- Q.24** What volume of 0.2 M NaOH solution is needed for complete neutralisation of 0.49 gm orthophosphoric acid -
 (A) 75 ml (B) 300 ml (C) 0.075 ml (D) 50 ml
- Q.25** 34 g of hydrogen peroxide is present in 1135 mL of solution. Volume strength of solution is:
 (A) 10 V (B) 20 V (C) 30 V (D) 32 V
- Q.26** Label an oleum sample which has mass fraction of SO_3 equal to 0.6 :
 (A) 115 % (B) 109 % (C) 104.5 % (D) 113.5 %
- Q.27** If 50 gm oleum sample rated as 118% is mixed with 18 gm water, then the correct option is
 (A) The resulting solution contains 18 gm of water and 118 gm H_2SO_4
 (B) The resulting solution contains 9 gm water and 59 gm H_2SO_4
 (C) The resulting solution contains only 118 gm pure H_2SO_4
 (D) The resulting solution contains 68 gm of pure H_2SO_4

Q.28 12.5gm of fuming H_2SO_4 (labelled as 112%) is mixed with 100 lit water. Molar concentration of H^+ in resultant solution is :

[Note : Assume that H_2SO_4 dissociate completely and there is no change in volume on mixing]

- (A) $\frac{2}{700}$ (B) $\frac{2}{350}$ (C) $\frac{3}{350}$ (D) $\frac{3}{700}$

Q.29 20 ml of '20 vol' H_2O_2 solution is diluted to 80 ml. The final volume strength of solution is -

- (A) '80 vol' (B) '25 vol' (C) '5 vol' (D) '8 vol'

Q.30 Assuming complete precipitation of AgCl , calculate the sum of the molar concentration of all the ions if 2 lit of 2M Ag_2SO_4 is mixed with 4 lit of 1 M NaCl solution is :

- (A) 4M (B) 2M (C) 3 M (D) 2.5 M

Q.31 Molarity and Molality of a solute (M. wt = 50) in aqueous solution is 9 and 18 respectively. What is the density of solution.

- (A) 1 g/cc (B) 0.95 g/cc (C) 1.05 g/cc (D) 0.662 g/cc

Q.32 The relationship between mole fraction (X_A) of the solute & molality 'm' of its solution in ammonia would be

(A) $\frac{55.56(X_A)}{1 - X_A} = m$ (B) $\frac{58.82(X_A)}{1 - X_A} = m$

(C) $\frac{58.82(1 - X_A)}{X_A} = m$ (D) $\frac{55.56(1 - X_A)}{X_A} = m$

Q.33 3.0 molal NaOH solution has a density of 1.12 g/mL. The molarity of the solution is-

- (A) 2.97 (B) 3 (C) 3.05 (D) 3.5

EXERCISE # O-II

Q.1 Statement -1 : Molality of pure ethanol is lesser than pure water.

Statement -2 : As density of ethanol is lesser than density of water.

[Given : $d_{\text{ethanol}} = 0.789 \text{ gm/ml}$; $d_{\text{water}} = 1 \text{ gm/ml}$]

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
- (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
- (C) Statement-1 is false, statement-2 is true.
- (D) Statement-1 is true, statement-2 is false.

Q.2 Statement-1 : Molarity and molality have almost same value for a very dilute aqueous solution.

Statement-2 : In all very dilute solution, the mass of solvent (in gm) is equal to the volume of solution (in ml).

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
- (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
- (C) Statement-1 is true, statement-2 is false.
- (D) Statement-1 is false, statement-2 is true.

Q.3 Statement-1 : Molarity of a solution depends on temperature but molality is independent of temperature.

Statement-2 : Molarity depends on volume of solution but molality depends on mass of solvent.

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
- (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
- (C) Statement-1 is true, statement-2 is false.
- (D) Statement-1 is false, statement-2 is true.

Q.4 Statement-1 : The mass fraction of solute in a solution is always greater than its mole fraction.

Statement-2 : Mole fraction of solvent in an aqueous solution of ethanol must be greater than that of solute.

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
- (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
- (C) Statement-1 is true, statement-2 is false.
- (D) Statement-1 is false, statement-2 is true.

- Q.5 Statement-1 :** 0.5 M - aq. NaOH solution is identical to 2% (w/v) aq. NaOH solution.
Statement-2 : Concentration in % (w/v) is 4 times the molar concentration for all aqueous solution.
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
 (C) Statement-1 is true, statement-2 is false.
 (D) Statement-1 is false, statement-2 is true.
- Q.6** The molar concentration of HCl (aq.) is 10^{-5} M. Which of the following statements are correct.
 ($d_{\text{solution}} = 1 \text{ gm/cc}$)
 (A) The mole fraction of HCl $\cong 1.8 \times 10^{-7}$
 (B) The concentration of HCl in ppm is 3.65 ppm
 (C) The molality of HCl solution is approximately 10^{-5} m
 (D) The (w/v)% of solution is $3.65 \times 10^{-5} \%$
- Q.7** Solution(s) containing 40 gm NaOH is/are
 (A) 50 gm of 80% (w/w) NaOH
 (B) 50 gm of 80% (w/v) NaOH [$d_{\text{soln.}} = 1.2 \text{ gm/ml}$]
 (C) 50 gm of 20 M NaOH [$d_{\text{soln.}} = 1 \text{ gm/ml}$]
 (D) 50 gm of 5m NaOH
- Q.8** The **incorrect** statement(s) regarding 2M MgCl_2 aqueous solution is/are ($d_{\text{solution}} = 1.09 \text{ gm/ml}$)
 (A) Molality of Cl^- is **4.44 m**
 (B) Mole fraction of MgCl_2 is exactly **0.035**
 (C) The conc. of MgCl_2 is **19% w/v**
 (D) The conc. of MgCl_2 is **19×10^4 ppm**
- Q.9** A sample of H_2O_2 solution labelled as 56.75 volume has density of 530 gm/L. Mark the correct option(s) representing concentration of same solution in other units. (Solution contains only H_2O and H_2O_2)
 (A) $M_{\text{H}_2\text{O}_2} = 6$ (B) $\% \frac{w}{v} = 17$
 (C) Mole fraction of $\text{H}_2\text{O}_2 = 0.25$ (D) $m_{\text{H}_2\text{O}_2} = \frac{1000}{72}$
- Q.10** 100 mL of 0.06 M $\text{Ca}(\text{NO}_3)_2$ is added to 50 mL of 0.06 M $\text{Na}_2\text{C}_2\text{O}_4$. After the reaction is complete (CaC_2O_4 is precipitated)
 (A) 0.003 moles of calcium oxalate will get precipitated
 (B) 0.003 M Ca^{2+} will remain in excess
 (C) $\text{Na}_2\text{C}_2\text{O}_4$ is the limiting reagent
 (D) Oxalate ion ($\text{C}_2\text{O}_4^{2-}$) concentration in final solution is 0.003 M

Comprehension Q.11 and Q.12 (2 questions)

2 litre of 9.8 % w/w H_2SO_4 ($d = 1.5 \text{ gm/ml}$) solution is mixed with 3 litre of 1 M KOH solution.

- Q.11** The number of moles H_2SO_4 added are
 (A) 1 (B) 2 (C) 3 (D) 0.5
- Q.12** The concentration of H^+ if solution is acidic or concentration of OH^- if solution is basic in the final solution is
 (A) 0 (B) $\frac{3}{10}$ (C) $\frac{3}{5}$ (D) $\frac{2}{5}$

Comprehension Q.13 and Q.14 (2 questions)

30 gm H_2SO_4 is mixed with 20 gram SO_3 to form mixture.

- Q.13** Find mole fraction of SO_3 .
 (A) 0.2 (B) 0.45 (C) 0.6 (D) 0.8
- Q.14** Determine % labelling of oleum solution.
 (A) 104.5 (B) 106 (C) 109 (D) 110

Comprehension Q.15 and Q.16 (2 questions)**Estimation of halogens :**

Carius method : A known mass of compound is heated with conc. HNO_3 in the presence of AgNO_3 contained in a hard glass tube known as carius tube in a furnace. C and H are oxidised to CO_2 and H_2O . The halogen forms the corresponding AgX . It is filtered, dried, and weighed.

Estimation of sulphur : A known mass of compound is heated with fuming HNO_3 or sodium peroxide (Na_2O_2) in the presence of BaCl_2 solution in Carius tube. Sulphur is oxidised to H_2SO_4 and precipitated as BaSO_4 . It is filtered, dried and weighed.

- Q.15** 0.15 gm of an organic compound gave 0.12 gm of silver bromide by the Carius method. Find the percentage of bromine in the compound. ($\text{Ag} = 108$, $\text{Br} = 80$)
 (A) 34.0 (B) 46.0 (C) 80.0 (D) 50.0
- Q.16** 0.32 gm of an organic substance when treated by Carius method gave 0.466 gm of BaSO_4 . Calculate the percentage of sulphur in the compound. ($\text{Ba} = 137$)
 (A) 10.0 (B) 34.0 (C) 20.0 (D) 30.0

Comprehension Q.17 and Q.18 (2 questions)**(d) Estimation of phosphorous :**

A known mass of compound is heated with fuming HNO_3 or sodium peroxide (Na_2O_2) in Carius tube which converts phosphorous to H_3PO_4 . Magnesia mixture ($\text{MgCl}_2 + \text{NH}_4\text{Cl}$) is then added, which gives the precipitate of magnesium ammonium phosphate (MgNH_4PO_4) which on heating gives magnesium pyrophosphate ($\text{Mg}_2\text{P}_2\text{O}_7$), which is weighed.

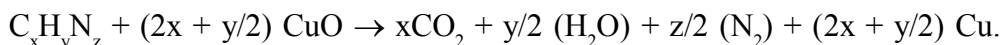
- Q.17** 0.124 gm of an organic compound containing phosphorus gave 0.222 gm of $\text{Mg}_2\text{P}_2\text{O}_7$ by the usual analysis. Calculate the percentage of phosphorous in the compound. ($\text{Mg} = 24$, $\text{P} = 31$)
 (A) 25 (B) 75 (C) 62 (D) 50

- Q.18** An organic compound has 6.2 % of phosphorus. On sequence of reaction, the phosphorous present in the 10gm of organic compound is converted to $\text{Mg}_2\text{P}_2\text{O}_7$. Find the weight of $\text{Mg}_2\text{P}_2\text{O}_7$ formed.
- (A) 2.22 gm (B) 10.0 gm (C) 4.44 gm (D) 1.11 gm

Comprehension Q.19 and Q.22 (4 questions)

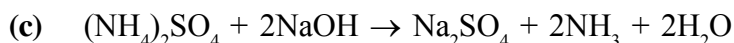
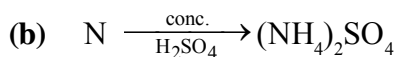
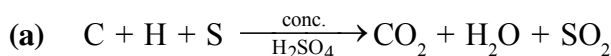
Estimation of nitrogen : There are two methods for the estimation of nitrogen (i) Dumas method and (ii) Kjeldahl's method.

- i. Dumas method :** A known mass of compound is heated with copper oxide (CuO) in an atmosphere of CO_2 , which gives free nitrogen along with CO_2 and H_2O .



The gaseous mixture is passed over a heated copper gauze which converts traces of nitrogen oxides formed to N_2 . The gaseous mixture is collected over an aqueous solution of KOH which absorbs CO_2 , and nitrogen is collected in the upper part of the graduated tube.

- ii. Kjeldahl's method :** A known mass of organic compound (0.5 gm) is mixed with K_2SO_4 (10 gm) and CuSO_4 (1.0 gm) or a drop of mercury (Hg) and conc. H_2SO_4 (25 ml), and heated in Kjeldahl's flask. CuSO_4 or Hg acts as a catalyst, while K_2SO_4 raises the boiling point of H_2SO_4 . The nitrogen in the organic compound is quantitatively converted to ammonium sulphate. The resulting mixture is then distilled with excess of NaOH solution and the NH_3 evolved is passed into a known but excess volume of standard HCl or H_2SO_4 . The acid left unused is estimated by titration with some standard alkali. The amount of acid used against NH_3 can thus be known and from this the percentage of nitrogen is calculated.



- iii.** This method is not applicable to compounds containing N in nitro and azo groups, and N present in the ring (e.g., pyridine) as N of these compounds does not change to $(\text{NH}_4)_2\text{SO}_4$ (ammonium sulphate) under these reaction conditions.

- Q.19** 0.30 gm of an organic compound gave 82.1 ml of nitrogen collected at 300K and 775 mm pressure in Dumas method. Calculate the percentage of nitrogen in the compound. (Vapour pressure of water or aqueous tension of water at 300K is 15 mm.

(A) 31.11 (B) 15.56 (C) 28.0 (D) 31.72

- Q.20** 0.50 gm of an organic compound was treated according to Kjeldahl's method. The ammonia evolved was absorbed in 50 ml of 0.5M H_2SO_4 . The residual acid required 60 ml of M/2 NaOH solution. Find the percentage of nitrogen in the compound.

(A) 50 (B) 56 (C) 66 (D) 40

- Q.21** 0.4 gm of an organic compound was treated according to Kjeldahl's method. The ammonia evolved was absorbed in 50 ml of 0.5M H_3PO_3 . The residual acid required 30 ml of 0.5M $\text{Ca}(\text{OH})_2$. Find the percentage of N_2 in the compound.

(A) 20 (B) 50 (C) 70 (D) 45

Q.22 0.002 gm of an organic compound was treated according to Kjeldahl's method. 0.2×10^{-4} mol of H_2SO_4 was required to neutralise NH_3 . Calculate the percentage of N_2 .

- (A) 50 (B) 28 (C) 70 (D) 18

TABLE TYPE QUESTION

Column-I	Column-II	Column-III
(A) 2 M - aqueous NaOH solution (density = 1.25 gm/ml)	(P) 2 mole solute/litre solution	(I) 6 % (w/v) solution
(B) 1.5 m - aqueous NaOH solution (density = 1.06 gm/ml)	(Q) 1.5 mole solute/litre solution	(II) 8 % (w/v) solution
(C) 0.5 M aqueous Glucose solution (density = 1.09 gm/ml)	(R) 0.5 mole solute/litre solution	(III) 9 % (w/v) solution
(D) 1.5 M aqueous Urea solution (density = 1.15 gm/ml)	(S) 1.5 mole solute/kg solvent	(IV) 9 gm solute per 100 gm solvent

Q.23 Which of the following is correct match ?

- (A) A – P – II (B) B – Q – I (C) C – R – IV (D) D – S – III

Q.24 Which of the following is correct match ?

- (A) A – P – II (B) B – S – I (C) C – R – I (D) D – Q – I

Q.25 Which of the following is correct match ?

- (A) A – Q – III (B) B – Q – III (C) C – Q – III (D) D – Q – III

MATCH THE COLUMN :

Q.26 Match the column-

Column-I (Concentration of aqueous solution)	Column-II (Density of given solutions is 1.2 g/ml)
(A) 2M NaOH solution	(P) 16gm solute in 240gm solution
(B) $8\% \left(\frac{w}{v} \right)$ KOH solution	(Q) 60gm solute in 240 gm solution
(C) $25\% \left(\frac{w}{W} \right)$ CaCO_3 solution	(R) 8gm solute in 100 ml solution
(D) $X_{\text{C}_3\text{H}_7\text{OH}} = \frac{1}{11}$	(S) 30 gm solute in 100 ml solution
	(T) 1 mole solute in 400 gm solution

Q.27 Match the column:

Column I	Column II
(A) 20 V H_2O_2	(P) 2.5 M
(B) 24.5 % w/v H_2SO_4	(Q) 1.76 M
(C) Pure water	(R) 1.5 M
(D) 5% w/w NaOH ($d_{\text{solution}} = 1.2 \text{ gm/ml}$)	(S) 55.5 M

Q.28

Column-I	Column-II
(A) 120 g CH_3COOH in 1 L solution ($d_{\text{sol}} = 1.2 \text{ g/mL}$)	(P) $M = 2$
(B) 120 g glucose dissolved in 1 L solution ($d_{\text{sol}} = 1.2 \text{ g/mL}$)	(Q) 10% w/w solution
(C) $X_{\text{NH}_2\text{CONH}_2} = 1/31$ (aqueous solution)	(R) 12% w/v solution
(D) 19.6% (w/v) H_2SO_4 solution \rightarrow ($d_{\text{solution}} = 1.2 \text{ g/mL}$)	(S) $m = 1.85$ (T) $m = 0.617$

EXERCISE : J-MAINS

1. 6.02×10^{21} molecules of urea are present in 100 ml of its solution. The concentration of urea solution is - [AIEEE-2004]
 (1) 0.001 M (2) 0.01 M (3) 0.02 M (4) 0.1 M
2. A 5.2 molal aqueous solution of methyl alcohol, CH_3OH , is supplied. What is the mole fraction of methyl alcohol in the solution ? [AIEEE-2011]
 (1) 0.086 (2) 0.050 (3) 0.100 (4) 0.190
3. The concentrated sulphuric acid that is peddled commercially is 95% H_2SO_4 by weight. If the density of this commercial acid is 1.834 g cm^{-3} , the molarity of this solution is :- [JEE-(Main)-2012]
 (1) 17.8 M (2) 15.7 M (3) 10.5 M (4) 12.0 M
4. The density of a solution prepared by dissolving 120 g of urea (mol. mass = 60 u) in 1000 g of water is 1.15 g/mL . The molarity of this solution is [JEE-(Main)-2012]
 (1) 2.05 M (2) 0.50 M (3) 1.78 M (4) 1.02 M
5. 10 mL of 2(M) NaOH solution is added to 200 mL of 0.5 (M) of NaOH solution. What is the final concentration ? [JEE(Main-online)-2013]
 (1) 0.57 M (2) 5.7 M (3) 11.4 M (4) 1.14 M
6. The density of 3M solution of sodium chloride is 1.252 g mL^{-1} . The molality of the solution will be (molar mass, $\text{NaCl} = 58.5 \text{ g mol}^{-1}$) [JEE(Main-online)-2013]
 (1) 2.18 m (2) 3.00 m (3) 2.60 m (4) 2.79 m
7. The amount of BaSO_4 formed upon mixing 100 mL of 20.8% BaCl_2 solution with 50 mL of 9.8% H_2SO_4 solution will be : [JEE(Main-online)-2014]
 (Ba = 137, Cl = 35.5, S=32, H = 1 and O = 16)
 (1) 33.2 g (2) 11.65 g (3) 23.3 g (4) 30.6 g
8. For the estimation of nitrogen, 1.4 g of an organic compound was digested by Kjeldahl method and the evolved ammonia was absorbed in 60 mL of $\frac{\text{M}}{10}$ sulphuric acid. The unreacted acid required 20 mL of $\frac{\text{M}}{10}$ sodium hydroxide for complete neutralization. The percentage of nitrogen in the compound is : [JEE(Main-online)-2014]
 (1) 3% (2) 5% (3) 6% (4) 10%

EXERCISE # J-ADVANCE

- Q.1** Calculate the molarity of pure water using its density to be 1000 kg m^{-3} . [JEE'2003]
- Q.2** Dissolving 120 g of urea (mol. wt. 60) in 1000 g of water gave a solution of density 1.15 g/mL . The molarity of the solution is
(A) 1.78 M (B) 2.00 M (C) 2.05 M (D) 2.22 M [JEE 2011]
- Q.3** A compound H_2X with molar weight of 80 g is dissolved in a solvent having density of 0.4 g /ml , Assuming no change in volume upon dissolution, the **molality** of a 3.2 molar solution is. [JEE 2014]

ANSWER-KEY

EXERCISE # S-I

Q.1 (a) 0.5 M, (b) 0.5 M, (c) 0.2 M	Q.2 1.3 M	Q.3 2.4M
Q.4 16.66%	Q.5 3.0×10^{-4}	Q.6 1.4
Q.7 0.15 M	Q.8 0.06 M	Q.9 1.25 gm/ml
Q.10 45.45%	Q.11 2.5×10^{-3} M	Q.12 0.01 M
Q.13 13 gm	Q.14 0.6667, 0.6667	Q.14 (1)
Q.16 1.4 litre	Q.17 175 ml	Q.18 2 M
Q.19 1.5 ml	Q.20 (0.8)	Q.21 0.05
Q.22 0.204 M	Q.23 5.56 ml	Q.24 (0.15)
Q.25 (1.5)		
Q.26 (i) 20 gm ; (ii) 35.4 gm ; (iii) $\text{H}_2\text{SO}_4 = 35.4$ gm, $\text{H}_2\text{O} = 34.6$ gm		
Q.27 (a) 0.169; (b) 118 %	Q.28 45.4 V	Q.29 (6)
Q.30 (56)		

EXERCISE # S-II

Q.1 Ans.250	Q.2 Ans.25 ml	Q.3 Ans.5
Q.4 Ans.0.5	Q.5 Ans.60	Q.6 Ans.0.05
Q.7 Ans.3.33 m	Q.8 Ans.(12)	Q.9 Ans.(2)
Q.10 Ans. (2)		

EXERCISE # O-I

Q.1 Ans.(A)	Q.2 Ans.(C)	Q.3 Ans.(D)
Q.4 Ans.(B)	Q.5 Ans.(C)	Q.6 Ans.(A)
Q.7 Ans.(B)	Q.8 Ans.(D)	Q.9 Ans.(B)
Q.10 Ans.(B)	Q.11 Ans.(D)	Q.12 Ans.(D)
Q.13 Ans.(C)	Q.14 Ans.(B)	Q.15 Ans.(C)
Q.16 Ans.(D)	Q.17 Ans.(B)	Q.18 Ans.(C)
Q.19 Ans.(A)	Q.20 Ans. (A)	Q.21 Ans.(C)
Q.22. Ans.(C)	Q.23 Ans.(C)	Q.24 Ans.(A)
Q.25 Ans.(A)	Q.26 Ans.(D)	Q.27 Ans.(B)
Q.28 Ans.(A)	Q.29 Ans.(C)	Q.30 Ans.(B)
Q.31 Ans.(B)	Q.32 Ans.(B)	
Q.33 Ans.(B)		

EXERCISE # O-II

- | | | |
|---|---------------|------------------|
| Q.1 Ans.(B) | Q.2 Ans. (C) | Q.3 Ans. (A) |
| Q.4 Ans. (D) | Q.5 Ans. (C) | Q.6 Ans. (A,C,D) |
| Q.7 Ans.(A,C) | Q.8 Ans.(B,D) | Q.9 Ans.(B,D) |
| Q.10 Ans.(A,C) | Q.11 Ans.(C) | Q.12 Ans.(C) |
| Q.13 Ans.(B) | Q.14 Ans.(C) | Q.15 Ans.(A) |
| Q.16 Ans.(C) | Q.17 Ans.(D) | Q.18 Ans.(A) |
| Q.19 Ans.(A) | Q.20 Ans.(B) | Q.21 Ans.(C) |
| Q.22 Ans.(B) | Q.23 Ans.(A) | Q.24 Ans.(B) |
| Q.25 Ans.(D) | | |
| Q.26 Ans.(A) - P, R ; (B) - P, R ; (C) - Q, S, T ; (D) - S, Q | | |
| Q.27 Ans.(A) - Q ; (B) - P ; (C) - S ; (D) - R | | |
| Q.28. Ans.(A) - P,Q,R,S ; (B) - Q,R,T ; (C) - Q,S ; (D) - P | | |

EXERCISE # J-MAINS

- | | | |
|------------|------------|------------|
| 1. Ans.(4) | 2. Ans.(1) | 3. Ans.(1) |
| 4. Ans.(1) | 5. Ans.(1) | 6. Ans.(4) |
| 7. Ans.(2) | 8. Ans.(4) | |

EXERCISE # J-ADVANCE

- | | | |
|----------------------------------|-------------|-------------|
| Q.1 Ans.55.5 mol L ⁻¹ | Q.2 Ans.(C) | Q.3 Ans.(8) |
|----------------------------------|-------------|-------------|

Important Notes

NURTURE COURSE

EUDIOMETRY

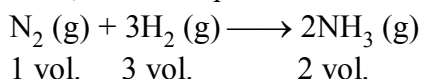
EUDIOMETRY

KEY CONCEPTS

EUDIOMETRY :

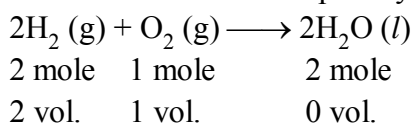
Eudiometry or gas analysis involves the calculations based on gaseous reactions or the reactions in which at least two components are gaseous, in which the amounts of gases are represented by their volumes, measured at the same pressure and temperature. Some basic assumptions related with calculations are:

1. Gay-Lussac's law of volume combination holds good. According to this law, the volumes of gaseous reactants reacted and the volumes of gaseous products formed, all measured at the same temperature and pressure, bear a simple ratio.



Problem may be solved directly in terms of volume, in place of mole. The stoichiometric coefficients of a balanced chemical reaction gives the ratio of volumes in which gaseous substances are reacting and products are formed, at same temperature and pressure.

2. The volumes of solids or liquids is considered to be negligible in comparison to the volume of gas. It is due to the fact that the volume occupied by any substance in gaseous state is even more than thousand times the volume occupied by the same substance in solid or liquid states.



3. Air is considered as a mixture of oxygen and nitrogen gases only. It is due to the fact that about 99% volume of air is composed of oxygen and nitrogen gases only.
4. Nitrogen gas is considered as a non-reactive gas. It is due to the fact that nitrogen gas reacts only at very high temperature due to its very high thermal stability. Eudiometry is performed in an eudiometer tube and the tube can not withstand very high temperature. This is why, nitrogen gas can not participate in the reactions occurring in the eudiometer tube.
5. The total volume of non-reacting gaseous mixture is equal to sum of partial volumes of the component gases (*Amagat's law*).

$$V = V_1 + V_2 + \dots$$

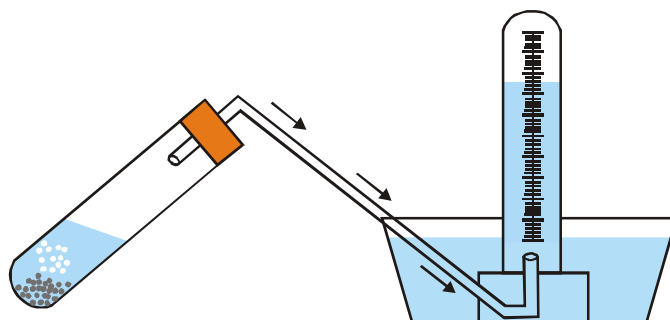
Partial volume of gas in a non-reacting gaseous mixture is its volume when the entire pressure of the mixture is supposed to be exerted only by that gas.

6. The volume of gases produced is often given by certain solvent which absorb contain gases.

Solvent	Gases absorb
KOH	CO ₂ , SO ₂ , Cl ₂
Ammonical Cu ₂ Cl ₂	CO
Turpentine oil	O ₃
Alkaline pyrogallol	O ₂
water	NH ₃ , HCl
CuSO ₄ /CaCl ₂	H ₂ O

EUDIOMETER

An eudiometer is a laboratory device that measures the change in volume of a gas mixture following a physical or chemical change.

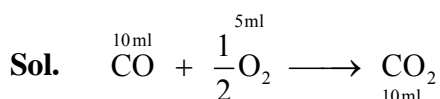


Scheme of eudiometer

To use a eudiometer, it is filled with water, inverted so that its open end is facing the ground (while holding the open end so that no water escapes), and then submersed in a basin of water. A chemical reaction is taking place through which gas is created. One reactant is typically at the bottom of the eudiometer (which flows downward when the eudiometer is inverted) and the other reactant is suspended on the rim of the eudiometer, typically by means of a platinum or copper wire (due to their low reactivity). When the gas created by the chemical reaction is released, it should rise into the eudiometer so that the experimenter may accurately read the volume of the gas produced at any given time. Normally a person would read the volume when the reaction is completed

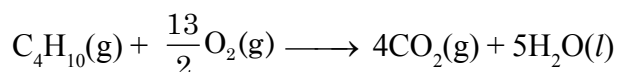
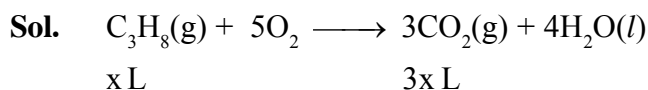
SOLVED EXAMPLE

Ex.1 10 ml of CO is mixed with 25 ml air (20% O₂ by volume) in a container at 1 atm. Find final volume (in ml) of container at 1 atm after complete combustion. (Assume that temperature remain constant).



$$V_f = V_{\text{CO}_2} + \text{Volume of remaining air} = 10 + 20 = 30 \text{ ml}$$

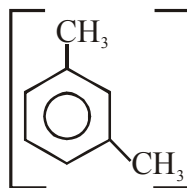
Ex.2 A 3 L gas mixture of propane (C₃H₈) and butane (C₄H₁₀) on complete combustion at 25°C produced 10 L CO₂. Assuming constant P and T conditions what was volume of butane present in initial mixture ?



from question $3x + 4(3-x) = 10 \Rightarrow x = 2$

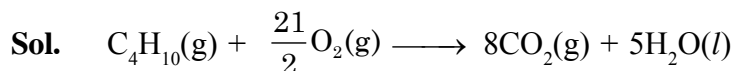
\therefore Volume of butane, C₄H₁₀ = (3 - x) = 1 L

Ex.3 100 ml gaseous meta Xylene



undergoes combustion with excess of oxygen at room

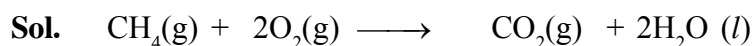
temperature and pressure. Volume contraction / expansion (in ml) during reaction is :



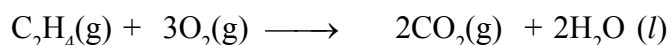
$$\begin{array}{ccccccc} 100 \text{ ml} & \frac{21}{2} \times 100 & & 800 \text{ ml} & & 0 & \\ & = 1050 \text{ ml} & & & & & \end{array}$$

$$\therefore \text{Contraction in volume} = (100 + 1050) - 800 = 350 \text{ ml}$$

Ex.4 30 ml gaseous mixture of methane and ethylene in volume ratio $X : Y$ requires 350 ml air containing 20% of O_2 by volume for complete combustion. If ratio of methane and ethylene changed to $Y : X$. What will be volume of air (in ml) required for complete reaction under similar condition of temperature and pressure.



$$V_1 \text{ ml} \quad 2V_1 \text{ ml} \quad V_1 \text{ ml} \quad 0$$



$$V_2 \text{ ml} \quad 3V_2 \text{ ml} \quad 2V_2 \text{ ml} \quad 0$$

$$\text{For given data : } V_1 + V_2 = 30$$

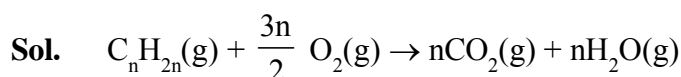
$$\text{and } 2V_1 + 3V_2 = 350 \times \frac{20}{100} = 70$$

$$\therefore V_1 = 20, V_2 = 10$$

$$\text{For required data : } V_1 = 10 \text{ and } V_2 = 20$$

$$\therefore \text{Volume of } \text{O}_2 \text{ required} = 2V_1 + 3V_2 = 80 \text{ ml} \text{ and volume of air required} = 80 = \frac{100}{20} = 400 \text{ ml}$$

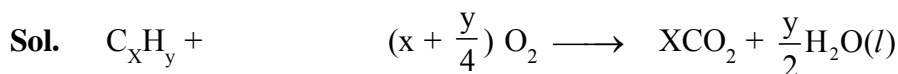
Ex.5 An alkene upon combustion produces $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$. In this combustion process if there is no volume change occurs then the no. of C atoms per molecule of alkene will be :



if there no volume changes i.e. $\Delta_{\text{ng}} = 0$

$$(n + n) - \left(1 + \frac{3n}{2}\right) = 0 \Rightarrow n = 2$$

Ex.6 A gaseous hydrocarbon (C_xH_y) requires 6 times of its own volume of O_2 for complete oxidation and produces 4 times of its volume of CO_2 . Find out the volume of $x + y$.



Vol a $a\left(x + \frac{y}{4}\right)$ ax

Given that : $a(x + y/4) = 6a$

vol of $CO_2 = 4$ vol of C_xH_y

$ax = 4(a)$

$x = 4$

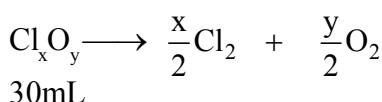
...(2)

from (1) $x + \frac{y}{4} = 6$

$\therefore x + y = 4 + 8 = 12$

Ex.7 On heating 60 ml mixture containing equal volume of chlorine gas and it's gaseous oxide, volume becomes 75 ml due complete decomposition of oxide. On treatment with KOH volume becomes 15 ml. What is the formula of oxide of chlorine ?

Sol. Let oxide of Cl is Cl_xO_y
So in 60 mL \Rightarrow 30 mL Cl_xO_y and 30 mL Cl_2 .
Now,



$\frac{30.x}{2}$ mL $\frac{30.y}{2}$ mL

Given :

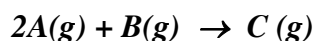
$75 = 30 + \frac{30x}{2} + \frac{30y}{2} \Rightarrow x + y = 3 \dots\dots\dots(i)$

KOH absorbs Cl_2 and volume becomes 15 mL so,

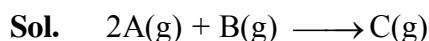
$(75 - 15) = V_{Cl_2} = 30 + \frac{30x}{2} \Rightarrow x = 2 \text{ and } y = 1$

So the oxide : Cl_2O

Ex.8 5 L of A (g) & 3 L of B(g) measured at same T & P are mixed together which react as follows



What will be the total volume (in litre) after the completion of the reaction at same T & P.



5L 3L

L.R. is A

So, volume of C produced = $\frac{1}{2} \times 5 = 2.5$ L

and, volume of B reacted = $\frac{1}{2} \times 5 = 2.5$ L

So, volume fo B remained = $3 - 2.5 = 0.5$ L

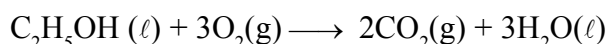
Hence, $V_{\text{total}} = V_C + V_B = 2.5 + 0.5 = 3$ L

EXERCISE # S-I

1. 20 ml propane gas (C_3H_8) is burnt completely in excess of air. The volume of CO_2 gas formed is.
2. What volume of $O_2(g)$ is needed for complete combustion of 40 ml ethane gas (C_2H_6) ?
3. 10 ml of CO is mixed with 25 ml air having 20% O_2 by volume. What would be the final volume if none of CO and O_2 is left after the reaction?
4. Calculate the volume of CO_2 evolved by the combustion of 50 ml of a mixture containing 40% C_2H_4 and 60% CH_4 (by volume)
5. 10 moles of a mixture of CO (g) and $CH_4(g)$ was mixed with 22 moles of O_2 gas and subjected to sparking. Find the moles of gas absorbed when the residual gases are passed through alc. KOH.
6. 60 ml of a mixture of nitrous oxide and nitric oxide was exploded with excess of hydrogen. If 38 ml of N_2 was formed, calculate the volume of NO gas in the mixture.
7. When 100 ml of a $O_2 - O_3$ mixture was passed through turpentine, there was reduction of volume by 20 ml. If 100 ml of such a mixture is heated, what will be the increase in volume?
8. 20 ml of a mixture of C_2H_2 and CO was exploded with 30 ml of oxygen. The gases after the reaction had a volume of 34 ml. On treatment with KOH, 8 ml of oxygen remained. Calculate the volume of C_2H_2 in the mixture.
9. 10 ml of a mixture of CO, CH_4 and N_2 exploded with excess of oxygen gave a contraction of 6.5 ml. There was a further contraction of 7 ml, when the residual gas treated with KOH. Volume of CO, CH_4 and N_2 respectively is
10. 10 ml of a mixture of CH_4 , C_2H_4 and CO_2 were exploded with excess of air. After explosion and further cooling, there was contraction of 17 ml and after treatment with KOH, there was further reduction of 14 ml. What is the composition of the mixture?
11. 10 ml of an oxide of nitrogen produce 20 ml NO_2 and 5 ml O_2 on complete decomposition. The oxide of nitrogen is-
12. Find the nature of hydrocarbon for which volume of oxygen required for combustion is 1.5 times volume of carbon dioxide produced.
13. A gaseous alkane is exploded with O_2 . The volume of O_2 required for complete combustion and the volume of CO_2 formed after combustion are in 7 : 4 ratio. What is the molecular formula of alkane ?
14. 20 ml of a gaseous hydrocarbon (A) was exploded with excess of O_2 in an eudiometer tube. On cooling, the volume was reduced by 50 ml. On further treatment with KOH, there was a further contraction of 40 ml. The molecular formula of hydrocarbon A is :
15. When a certain quantity of oxygen was ozonised in a suitable apparatus, the volume decreased by 4 ml. On addition of turpentine the volume further decreased by 8 ml. All volumes were measured at the same temperature and pressure. From these data, if formula of ozone is O_x then find x.

EXERCISE # S-II

1. A 20 ml mixture of C_2H_4 and C_2H_2 undergoes sparking in gas eudiometer with just sufficient amount of O_2 and shows contraction of 37.5 ml. Volume (in ml) of C_2H_2 in the mixture is.
2. 1120 ml of ozonised oxygen ($O_2 + O_3$) at 1 atm & 273K weighs 1.76 gm. Find the reduction in volume on passing this through alkaline pyrogallol solution is -
3. Balanced chemical equation is given as following :



What value of the volume in litre of CO_2 (g) measured at 200 K and 1 atm, produced from the combustion of 0.25 mole of C_2H_5OH (l) ? [Use $R = 0.08 \text{ L atm mol}^{-1} \text{ K}^{-1}$]

4. 40 ml of a mixture of C_2H_2 and CO is mixed with 100 ml of O_2 gas and the mixture is exploded. The residual gases occupied 104 ml and when these are passed through KOH solution, the volume becomes 48 ml. All the volume are at same temperature and pressure. Determine the composition of original mixture.
5. 10 mL of gaseous organic compound containing C, H and O only was mixed with 100 mL of O_2 and exploded under identical conditions and then cooled. The volume left after cooling was 90 mL. On treatment with KOH a contraction of 20 mL was observed. If vapour density of compound is 23, if molecular formula of the compound is $C_xH_yO_z$, then find $(x + y + z)$.

EXERCISE # O-I

Single correct

- 10 ml CH_4 gas is burnt completely in air ($\text{O}_2 = 20\%$, by volume). The minimum volume of air needed is -
(A) 20 ml (B) 50 ml (C) 80 ml (D) 100 ml
- 20 ml of a mixture of C_2H_4 and C_2H_6 gases is burnt completely in excess of O_2 . The volume of CO_2 gas formed is :
(A) 20 ml (B) 40 ml (C) 80 ml (D) 30 ml
- $\text{C}_6\text{H}_5\text{OH}(\text{g}) + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$
Magnitude of volume change if 30 ml of $\text{C}_6\text{H}_5\text{OH}(\text{g})$ is burnt with excess amount of oxygen, is
(A) 30 ml (B) 60 ml (C) 20 ml (D) 10 ml
- When 20 ml mixture of O_2 and O_3 is heated, the volume becomes 29 ml and disappears in alkaline pyragallol solution. What is the volume percent of O_2 in the original mixture?
(A) 90% (B) 10% (C) 18% (D) 2%
- The % by volume of C_4H_{10} in a gaseous mixture of C_4H_{10} , CH_4 and CO is 40. When 200 ml of the mixture is burnt in excess of O_2 . Find volume (in ml) of CO_2 produced.
(A) 220 (B) 340 (C) 440 (D) 560
- A mixture of C_2H_2 and C_3H_8 occupied a certain volume at 80 mm Hg. The mixture was completely burnt to CO_2 and $\text{H}_2\text{O}(\text{l})$. The pressure of CO_2 was found to be 230 mm Hg at the same temperature and volume. The fraction of C_2H_2 in mixture is
(A) 0.125 (B) 0.5 (C) 0.85 (D) 0.25
- 20 mL of a mixture of CO and H_2 were mixed with excess of O_2 and exploded & cooled. There was a volume contraction of 23 mL. All volume measurements corresponds to room temperature (27°C) and one atmospheric pressure. Determine the volume ratio $V_1 : V_2$ of CO and H_2 in the original mixture
(A) 6.5 : 13.5 (B) 5 : 15 (C) 9 : 11 (D) 7 : 13
- An ideal gaseous mixture of ethane (C_2H_6) and ethene (C_2H_4) occupies 28 litre at 1 atm, 0°C . The mixture reacts completely with 128 gm O_2 to produce CO_2 and H_2O . Mole fraction of C_2H_6 in the mixture is—
(A) 0.6 (B) 0.4 (C) 0.5 (D) 0.8
- For a chemical reaction occurring at constant pressure and temperature.
 $2\text{A}(\text{g}) + 5\text{B}(\text{g}) \longrightarrow \text{C}(\text{g}) + 2\text{D}(\text{g})$
(A) contraction in volume is double the volume of A taken if B is taken in excess.
(B) contraction in volume is more than the volume of B taken if A is in excess.
(C) volume contracts by 20 mL if 10 mL A is reacted with 20 mL B.
(D) no change in volume due to reaction

10. One litre of CO_2 passed over hot coke the volume becomes 1.4 litres then the composition of products will not be (At NTP)
- (A) $V_{\text{CO}_2} : V_{\text{CO}} = 3 : 4$ (B) $V_{\text{CO}_2} = 1.6 \text{ ltr.}$ (C) $n_{\text{CO}_2} : n_{\text{CO}} = 3 : 4$ (D) $\% V \text{ of CO} = \frac{400}{7}$
11. 10 ml of a compound containing 'N' and 'O' is mixed with 30 ml of H_2 to produce H_2O (l) and 10 ml of N_2 (g). Molecular formula of compound if both reactants reacts completely, is
- (A) N_2O (B) NO_2 (C) N_2O_3 (D) N_2O_5
12. An alkane on complete combustion with O_2 shows 50% of volume contraction. Molecular formula of alkane is -
- (A) C_4H_{10} (g) (B) CH_4 (g) (C) C_2H_6 (g) (D) C_3H_8 (g)
13. 20 mL of a gaseous hydrocarbon was exploded with 120 mL of oxygen. A contraction of 60 mL was observed, and a further contraction of 60 mL took place when KOH was added. What is the formula of the hydrocarbon :
- (A) C_3H_6 (B) C_3H_8 (C) C_2H_6 (D) C_4H_{10}
14. When a definite volume of a gaseous alkyne ($\text{C}_n\text{H}_{2n-2}$) is burnt completely in excess of air, a contraction in volume equal to twice the volume of alkyne burnt occurred. The value of 'n' is -
- (A) 10 (B) 6 (C) 3 (D) 20
15. Each volume of a gaseous organic compound containing C, H and S only produce 1 volume CO_2 , 2 volume H_2O vapours and 1 volume SO_2 gases on complete combustion. The molecular formula of compound is -
- (A) CH_2S (B) CH_4S (C) $\text{C}_2\text{H}_4\text{S}$ (D) $\text{C}_2\text{H}_6\text{S}$

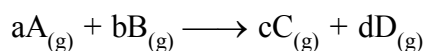
EXERCISE # O-II

Single correct :

1. A 2 L sample of a gaseous hydrocarbon is burnt in excess oxygen. The only products of the reaction are 8L of $\text{CO}_2(\text{g})$ and 10L of $\text{H}_2\text{O}(\text{g})$, all at 100°C and 1 atm pressure. The formula of the hydrocarbon is -
 (A) C_5H_{12} (B) C_4H_5 (C) C_4H_{10} (D) C_8H_{10}
2. 1120 ml of ozonised oxygen ($\text{O}_2 + \text{O}_3$) at 1 atm & 273K weighs 1.76 gm. The reduction in volume on passing this through alkaline pyrogallol solution is -
 (A) 896 ml (B) 224 ml (C) 448 ml (D) 672 ml
3. **Statement-1 :** When a gaseous hydrocarbon is burnt in excess of oxygen and the products of combustion are cooled to the original temperature and pressure, a contraction in volume occurs.
Statement-2 : The contraction in volume is solely due to the liquifaction of water vapour.
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
 (C) Statement-1 is true, statement-2 is false.
 (D) Statement-1 is false, statement-2 is true.
4. **Statement-1 :** For the same volume of gaseous alkane, alkene and alkyne having same number of carbon atoms, the volume of oxygen needed for complete combustion is maximum for alkane.
Statement-2 : The number of hydrogen atoms is maximum in alkane.
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
 (C) Statement-1 is true, statement-2 is false.
 (D) Statement-1 is false, statement-2 is true.

More than one correct:

5. Two gases A and B which react according to the equation



to give two gases C and D are taken (amount not known) in an Eudiometer tube (operating at a constant Pressure and temperature) to cause the above.

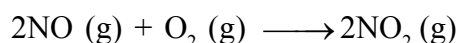
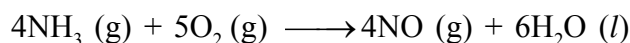
If on causing the reaction there is no volume change observed then which of the following statement is/are correct.

- (A) $(a + b) = (c + d)$
- (B) average molecular mass may increase or decrease if either of A or B is present in limited amount.
- (C) Vapour Density of the mixture will remain same throughout the course of reaction.
- (D) Total moles of all the component of mixture will change.

6. 20 ml mixture of C_3H_8 and CO gas when burnt in excess of oxygen produce 40 ml CO_2 gas. Choose the correct statement(s). (Volume of gases measured under same T & P)
- (A) Volume of C_3H_8 in the mixture is 15 ml
 (B) Volume of CO in the mixture is 10 ml
 (C) Total volume contraction due to combustion is 35 ml.
 (D) The volume of oxygen used for combustion is 75 ml
7. 10 ml of a gaseous mixture containing C_2H_x and C_3H_8 exactly requires 40 ml O_2 for complete combustion and produces 25 ml CO_2 and 30 ml H_2O vapour. The correct information (s) is/are -
- (A) Total volume contraction = 5 ml
 (B) Volume contraction due to combustion of $C_2H_x = 0$
 (C) $x = 4$
 (D) Volume of C_2H_x in the initial mixture = 5 ml
8. 100 ml mixture of CO and CO_2 mixed with 30 mL of O_2 and sparked in eudiometer tube. The residual gas after treatment with aq. KOH has a volume of 10 mL which remains unchanged when treated with alkaline pyrogallol. If all the volumes are under the same conditions, point out **correct** options(s):
- (A) The volume of CO that reacts, is 60 mL
 (B) The volume of CO that remains unreacted, is 10 mL
 (C) The volume of O_2 that remains unreacted, is 10 mL
 (D) The volume of CO_2 that gets absorbed by aq.KOH, is 90 mL.

Paragraph for Q.9 to Q.11

For the given series of reaction



9. If 20 ml of NH_3 is mixed with 100 ml of O_2 . Volume contraction at the completion of above reactions is
- (A) 20 ml (B) 85 ml (C) 35 ml (D) 100 ml
10. To obtain maximum mass of NO_2 from a given mass of a mixture of NH_3 and O_2 , the ratio of mass of NH_3 to O_2 should be
- (A) $\frac{4}{7}$ (B) $\frac{17}{56}$ (C) $\frac{17}{40}$ (D) None of these
11. Total volume of O_2 used if 20 ml NH_3 is mixed with 100 ml O_2
- (A) 40 (B) 60 (C) 35 (D) None of these

Table type question :

Column-I (Gas taken)	Column-II (O ₂ needed for complete combustion)	Column-III (Contraction in volume)
(1) 20 ml C ₂ H ₄	(i) 60 ml	(I) 50 ml
(2) 25 ml C ₃ H ₄	(ii) 100 ml	(II) 40 ml
(3) 30 ml C ₂ H ₆	(iii) 70 ml	(III) 75 ml
(4) 35 ml CH ₄	(iv) 105 ml	(IV) 70 ml

All volumes are measured at 25°C and 1 atm.

12. Which of the following is correct match -

- (A) 1 – i – II (B) 1 – iii – IV (C) 2 – iv – II (D) 2 – ii – III

13. Which of the following is correct match -

- (A) 3 – iii – III (B) 3 – iv – III (C) 4 – iii – III (D) 4 – iv – IV

14. Which of the following is incorrect (**One or more than one correct**)

- (A) 2 – ii – I (B) 4 – iii – IV (C) 3 – iv – IV (D) 1 – iii – II

Match the column :

15. Gaseous alkane (C_nH_{2n+2}) exploded with oxygen. Ratio of the mol of O₂ for complete combustion to the mole of CO₂ formed is given in column-I & in column II formula is given.

Column-I	Column-II
(A) 7 : 4	(P) C ₃ H ₈
(B) 2 : 1	(Q) C ₄ H ₁₀
(C) 5 : 3	(R) C ₂ H ₆
(D) 13 : 8	(S) CH ₄

ANSWER-KEY**EXERCISE # S-I**

- | | | |
|---|---|---------------|
| 1. Ans. 60 ml | 2. Ans. 140 ml | 3. Ans. 30 ml |
| 4. Ans. 70 ml | 5. Ans. (10) | |
| 6. Ans. NO = 44 ml ; N ₂ O = 16 ml | 7. Ans. 10 ml | |
| 8. Ans. C ₂ H ₂ = 6 ml, CO = 14 ml | 9. Ans. 5 ml, 2 ml, 3 ml | |
| 10. Ans. CH ₄ = 4.5 ml, CO ₂ = 1.5 ml | 11. Ans. (N ₂ O ₅) | |
| 12. Ans. (alkene) | 13. Ans. (C ₂ H ₆) | |
| 14. Ans. (C ₂ H ₆) | 15. Ans. (3) | |

EXERCISE # S-II

- | | | |
|--|------------------------------------|-------------|
| 1. Ans. (5) | 2. Ans. (896 ml) | 3. Ans. (8) |
| 4. C ₂ H ₂ = 16 ml, CO = 24 ml | 5. C ₂ H ₆ O | |

EXERCISE # O-I

- | | | |
|--------------|--------------|--------------|
| 1. Ans. (D) | 2. Ans. (2) | 3. Ans. (B) |
| 4. Ans. (B) | 5. Ans. (C) | 6. Ans. (A) |
| 7. Ans. (D) | 8. Ans. (B) | 9. Ans. (A) |
| 10. Ans. (B) | 11. Ans. (C) | 12. Ans. (D) |
| 13. Ans. (B) | 14. Ans. (C) | 15. Ans. (B) |

EXERCISE # O-II

- | | | |
|--|-----------------|---------------|
| 1. Ans. (C) | 2. Ans. (A) | 3. Ans. (C) |
| 4. Ans. (A) | 5. Ans. (A,C) | 6. Ans. (B,C) |
| 7. Ans. (B,C,D) | 8. Ans. (A,B,D) | 9. Ans. (C) |
| 10. Ans. (B) | 11. Ans. (C) | 12. Ans. (A) |
| 13. Ans. (B) | 14. Ans. (C,D) | |
| 15. Ans. A - R ; B - S ; C - P ; D - Q | | |

THERMODYNAMICS-01

Session 2019-20

ALLEN
Session 2019-20

THERMODYNAMICS-01

1. INTRODUCTION

Thermodynamics is concerned with energy and its transformation in various forms in different physical and chemical processes.

Thermodynamics \equiv Thermo + dynamics

Dynamics \equiv Study of change due to a driving force

Thermo \equiv Thermal which is related to temperature or energy.

The laws of thermodynamics deal with energy changes of macroscopic systems involving a large number of molecules rather than microscopic systems containing a few molecules. Thermodynamics is not concerned about how and at what rate these energy transformations are carried out, but is based on initial and final states of a system undergoing the change. Laws of thermodynamics apply only when a system is in equilibrium or moves from one equilibrium state to another equilibrium state. Macroscopic properties like pressure and temperature do not change with time for a system in equilibrium state.

2. SOME BASIC DEFINITIONS (Thermodynamic terms)

2.1 SYSTEM :

The macroscopic part of the universe under study is called a system. Rest of the universe outside the system is called surroundings. The actual or imaginary surface that separates the system from the surroundings is called the boundary.

However, the entire universe other than the system is not affected by the changes taking place in the system. Therefore, for all practical purposes, the surroundings are that portion of the remaining universe which can interact with the system. Usually, the region of space in the neighbourhood of the system constitutes its surroundings.

2.1.1 Types of boundary :

- (i) Real or imaginary
- (ii) Rigid (fixed) or movable (flexible)
- (iii) Permeable (allow mass transfer) or impermeable (does not allow mass transfer).
- (iv) Diathermal (allow heat transfer) or Adiabatic (does not allow heat transfer).

2.1.2 Types of systems :

- (i) **Isolated system** : A system is said to be isolated if it cannot exchange matter and energy with the surroundings. Example : coffee in a thermos flask.
- (ii) **Closed system** : A system is said to be closed if it can exchange energy but not matter. Example : Coffee in a closed stainless steel flask.
- (iii) **Open system** : A system is said to be open if it can exchange matter and energy. Example : A thermos flask or a steel flask if not closed.

Note : A perfectly isolated system is only a theoretical system.

- 2.2 **State of system** : A system is called in a particular state where all the macroscopic properties of the system have defined value.

2.3 Properties of system : The state of a system is defined by a particular set of its measurable quantities called properties. They can be categorised into extensive and intensive properties.

Intensive property is one whose value is independent of the size (or mass) of the system. An extensive property is one whose value depends on the size (or mass) of the system.

- * Extensive properties are additive but intensive properties are non additive.
- * Ratio of two extensive property gives as intensive property.

Extensive Properties

Volume
Number of moles
Mass
Free Energy (G)
Entropy (S)
Enthalpy (H)
Internal energy (E & U)
Heat capacity

Intensive Properties

Molar volume
Density
Refractive index
Surface tension
Viscosity
Free energy per mole
Specific heat
Pressure
Temperature
Boiling point, freezing point etc

2.4 State function or state variable : Variables like P, V, T are State Functions or State Variables because their values depend only on the present state of a system and not on how the state was reached

Condition for a function to be a state function :

- (i) If ϕ is state function, $\int_A^B d\phi = \phi_B - \phi_A$
- (ii) If ϕ is a state function, $\oint d\phi = 0$

2.5 Path function : Function which depend on the path, i.e. how the process is carried out e.g. work & heat.

2.6 Thermodynamic process : A thermodynamic process involves change of a system from one state to another state.

EXERCISE # I

1. Which of the following are extensive and which are intensive properties ?

Temperature, boiling point, melting point, pressure, density, viscosity, surface tension, refractive index, molar volume, free energy/mole, specific heat, Specific volume, Mass, Volume, number of moles, Heat capacity, internal energy, enthalpy, entropy, ΔG , concentration, dipole moment, pH, gas constant, vapour pressure, specific gravity, E.M.F. of the dry cell, molarity, molality.

Sol. Intensive property : Temperature, (boiling point, melting point), pressure, density, viscosity, surface tension, refractive index, molar volume, free energy/mole, specific heat, Specific volume, concentration, dipole moment, pH, gas constant, vapour pressure, specific gravity, E.M.F. of the dry cell, molarity, molality.

Extensive property : Mass, Volume, number of moles, Heat capacity, internal energy, enthalpy, entropy

2. Which of the following are state function & path function ?

Pressure, Volume, Enthalpy, Work, Heat, Gibbs energy, temperature, Internal energy, Entropy

Sol. State function : Pressure, volume, enthalpy, Gibbs energy, temperature, Internal energy, Entropy

Path function : Work, Heat

3. A state function is that :

- (A) which is used in thermochemistry
- (B) which obeys all laws of thermodynamics
- (C) quantity whose value depends only upon the state of the system
- (D) quantity which is used in measuring thermal change

Ans. (C)

4. Which amongst the following is an extensive property of the system -

- (A) Temperature
- (B) Volume
- (C) Viscosity
- (D) Refractive index

Ans. (B)

5. Which of the following is not a state function of thermodynamic system -

- (A) Internal energy(E)
- (B) Free energy(G)
- (C) Enthalpy(H)
- (D) Work(W)

Ans. (D)

6. What is true for a cyclic process

- (A) $W = 0$
- (B) $\Delta E = 0$
- (C) $\Delta H = 0$
- (D) B & C both

Ans. (D)

7. The internal energy change when a system goes from state A to B is 40 kJ/mole. If the system goes from A to B by a reversible path and returns to state A by an irreversible path what would be the net change in internal energy ?

[AIEEE-2003]

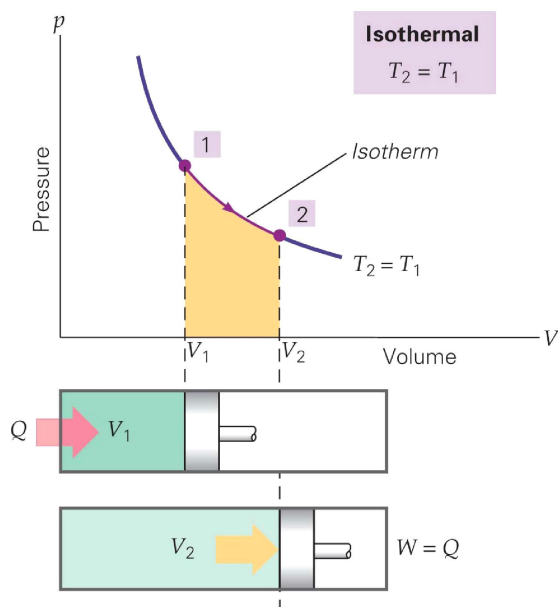
- (A) < 40 kJ
- (B) Zero
- (C) 40 kJ
- (D) > 40 kJ

Ans. (B)

Type of process :

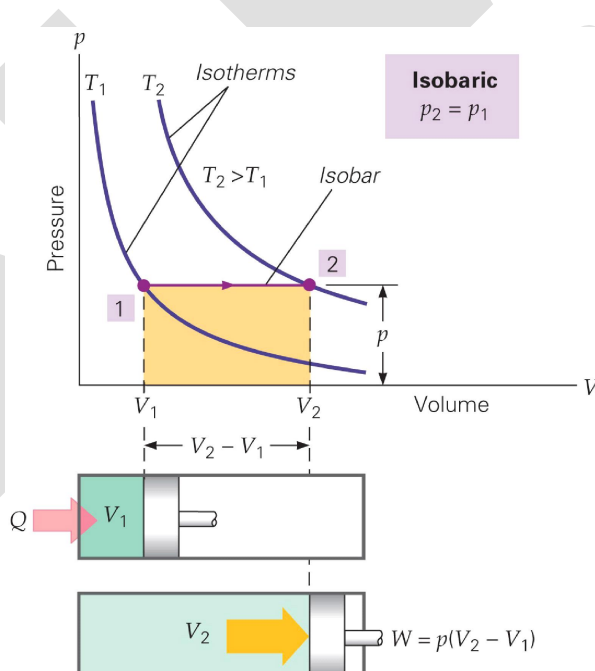
(i) **Isothermal process :**

A process in which temperature of the system remains constant is called isothermal process.



(ii) **Isobaric process :**

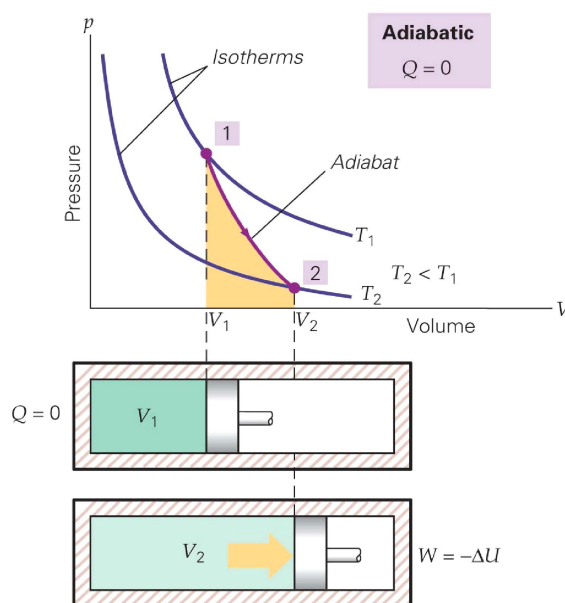
A process in which pressure of the system remains constant is called isobaric process. Temperature and volume of the system may change.



Ex. All the reactions or processes taking place in open vessel like boiling of water in open vessel, burning of charcoal, melting of wax take place at constant pressure (1 atm.)

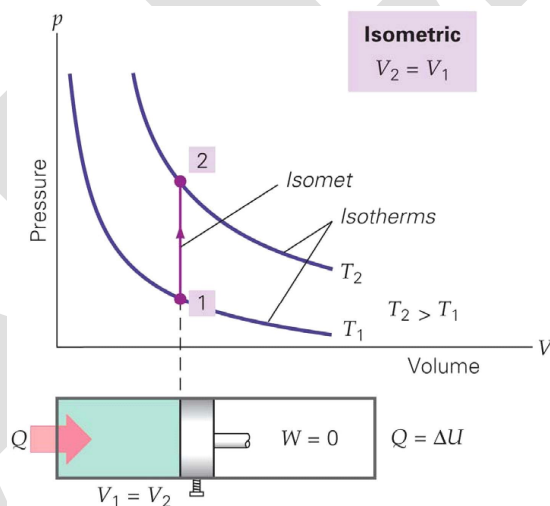
(iii) Adiabatic process :

A process in which no heat exchange takes place is called adiabatic process. Adiabatic process occurs in systems with insulated walls.



(iv) Isochoric process :

The process for which volume of the system remains constant is called isochoric process i.e., Heating of gas in closed or rigid vessel.



(v) **Cyclic process :** It is combination of two or more process in which the final state of system, becomes identical to the initial. The net change in all thermodynamic properties of system must be zero.

$$\Delta T = \Delta P = \Delta V = \Delta H = \Delta S = \Delta G \dots\dots\dots = 0$$

However Q_{net} or W_{net} may or may not be zero.

(vi) **Reversible or Irreversible process :** If the initial state may be received just by reversing the direction of process at any state, process is called reversible. In irreversible process the initial state can never be achieved just by reversing the direction of process.

In the reversible process, the driving force is only infinitesimally greater than the opposing force. In the irreversible process, they differ largely.

A perfectly reversible process is a theoretical process because it takes infinite time but reversible processes are important because it results maximum efficiency in any machine. The actual process occurring in the machine is quasi static which may tend to reversible or irreversible process.

During irreversible process, one of the equation of state like $PV = nRT$, is valid. Such equation is valid only at initial & final state. However during reversible process such equation are valid throughout the process.

A process is reversible when the system throughout remain in thermodynamic equilibrium with the surrounding. A system is said in thermodynamic equilibrium when it simultaneously satisfy the following equilibria.

- (a) **Thermal equilibrium:** Same temperature throughout (No heat transfer within the system)
- (b) **Mechanical equilibrium :** Same pressure or force throughout the system (No work should be performed by one part on the other)
- (c) **Material equilibrium :** No change in the composition of system with time. No mass transfer within the system.

If a system is in thermodynamic equilibrium there is no net energy or mass transfer within the system.

3. WORK

Thermodynamically, work may be defined as the form of energy which appears only when, there is some change in the boundary of the system. Such work is called mechanical or PV work.

Work may also be non-mechanical like electric work.

Presently, we will discuss only mechanical work.

- (i) It is not thermodynamic property of system.
- (ii) It depends on the quantity of system.
- (iii) Sign convention, work on system = (+)ve.

In physics, work is calculate from the force applied by system, but in chemistry due to external force.

$W = \int_{V_1}^{V_2} P \cdot dV = - \int_{V_1}^{V_2} P_{\text{ext}} dV$
<div style="display: flex; justify-content: space-around;"> Physics Chemistry </div>

4. HEAT

Heat is defined as the energy that flows into or out of a system because of a difference in temperature between the system and its surrounding.

According to IUPAC convention

heat lost by system is expressed with -ive sign

heat given to system is expressed with +ive sign

- * $q_v = nC_{v,m} dT$
- * $q_p = nC_{p,m} dT$
- * $C_{p,m} - C_{v,m} = R$ (for ideal gas)
- * C_v & C_p depends on temperature even for an ideal gas. ($C = a + bT + cT^2 \dots\dots\dots$)

General values of C_v & C_p for an ideal gas can be taken as follows.

Atomicity		n _{tr}	n _{Rot}	n _{Vib}	C _v		C _p		γ	
						Incl. Vib	Excl. Vib	Incl. Vib	Excl. Vib	Incl. Vib
Mono		3	0	0	$\frac{3}{2}R$	$\frac{3}{2}R$	$\frac{5}{2}R$	$\frac{5}{2}R$	$\frac{5}{3}$	$\frac{5}{3}$
Di		3	2	1	$\frac{5}{2}R$	$\frac{7}{2}R$	$\frac{7}{2}R$	$\frac{9}{2}R$	$\frac{7}{5}$	$\frac{9}{7}$
Tri	Linear	3	2	4	$\frac{5}{2}R$	$\frac{13}{2}R$	$\frac{7}{2}R$	$\frac{15}{2}R$	$\frac{7}{5}$	$\frac{15}{13}$
	Non Linear	3	3	3	3R	6R	4R	7R	$\frac{4}{3}$	$\frac{7}{6}$

5. INTERNAL ENERGY (E & U)

Every system having some quantity of matter is associated with a definite amount of energy, called internal energy.

$$U = U_{\text{Kinetics}} + U_{\text{Potential}} + U_{\text{Electronic}} + U_{\text{nuclear}} + \dots$$

U is a state function & is an extensive property.

$$\Delta U = U_{\text{final}} - U_{\text{initial}}$$

For a given closed system

$$U = f(T, V)$$

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV$$

6. ENTHALPY

Chemical reactions are generally carried out at constant pressure (atmospheric pressure) so it has been found useful to define a new state function **Enthalpy** (H) as.

$$H = U + PV$$

$$\Delta H = \Delta U + \Delta(PV)$$

at constant pressure

$$\Delta H = \Delta U + P \Delta V$$

combining with first law.

$$\Delta H = q_p$$

Hence transfer of heat at constant volume brings about a change in the internal energy of the system whereas that at constant pressure brings about a change in the enthalpy of the system.

6.1 RELATIONSHIP BETWEEN ΔH & ΔU :

The difference between ΔH & ΔU becomes significant only when gases are involved (insignificant in solids and liquids)

$$\Delta H = \Delta U + \Delta(PV)$$

If substance is not undergoing chemical reaction or phase change.

$$\Delta H = \Delta U + nR\Delta T$$

In case of chemical reaction

$$\Delta H = \Delta U + (\Delta n_g)RT$$

7. ZEROth LAW OF THERMODYNAMICS

Two system in thermal equilibrium with a third system are also in thermal equilibrium with each other. It introduces temperature as a state function.

8. FIRST LAW OF THERMODYNAMICS

"Total energy of universe remains constant." It is law of conservation of energy.

Let us consider a system whose internal energy is U_1 . If the system is supplied with heat q , the internal energy of the system increases to $U_1 + q$. If work (w) is done on the system, the internal energy in the final state of the system, U_2 is given by

$$U_2 = U_1 + q + w$$

$$\text{or } U_2 - U_1 = q + w$$

$$\Delta U = q + w$$

According to IUPAC, heat added to the system and work done on the system are assigned positive values as both these modes increase the internal energy of the system.

EXERCISE # II

8. Represent the following observations in terms of proper IUPAC symbol?

- Heat absorbed by a system is 20 Joule.
- Work done by a system is 40 Joule.
- Work done on a system is 5 Joule.
- Heat given out by system is 50 Joule.

Ans. It is standard practice to represent both types of heat and work (in/out or on/by) by single symbols q and w -

(a) $q = +20$ Joule.

(b) $w = -40$ Joule.

(c) $w = +5$ Joule.

(d) $q = -50$ Joule.

9. For certain processes the heat and work exchanged between system and surrounding is given in standard format. Describe the physical interpretation of each observation.

(a) $q = +10$ kJ

(b) $w = -20$ kJ

Ans. (a) $q = +10$ kJ :

Since numerical value of q is positive, this shows heat is absorbed by the system from surrounding resulting in gain of energy by system.

(b) $w = -20$ kJ :

Since numerical value of work is negative, this shows work is done by the system on surrounding resulting in loss of energy of system.

10. Predict sign of work done in following reactions at constant pressure.

Initial state		Final state
(i) $H_2O(g)$	\longrightarrow	$H_2O(l)$
(ii) $H_2O(s)$	\longrightarrow	$H_2O(g)$
(iii) $H_2O(l)$	\longrightarrow	$H_2O(s)$
(iv) $CaCO_3(s)$	\longrightarrow	$CaO(s) + CO_2(g)$

Ans. (i) +, (ii) -, (iii) -, (iv) -

11. Explain why variation of enthalpy for a process involving an ideal gas is given by $dH = nC_p dT$, irrespective of process ?

Sol. Because

$$H_{\text{ideal gas}} = f(T), \text{ independent of pressure or volume}$$

12. The heat capacity of a molecule depends upon complexity of the molecule. Explain ?

Sol. The heat capacity can be defined as energy needed to raise the temperature of a body by 1°C . The molecule which have large number of degree's of freedom requires larger quantity of heat to raise the temperature by 1°C . This is because energy supplied is distributed in each degree of freedom equally.

13. If work done by the system is 300 joule when 100 cal heat is supplied to it. The change in internal energy during the process is :-

- (A) -200 Joule
(B) 400 Joule
(C) 720 Joule
(D) 120 Joule

Ans. (D)

14. One mole of a gas absorbs 200J of heat at constant volume. Its temperature rises from 298 K to 308 K. The change in internal energy is :-

- (A) 200 J (B) -200 J (C) $200 \times \frac{308}{298}$ J (D) $200 \times \frac{298}{308}$ J

Ans. (A)

15. A system has internal energy equal to U_1 , 450 J of heat is taken out of it and 600 J of work is done on it. The final energy of the system will be -

- (A) $(U_1 + 150 \text{ J})$ (B) $(U_1 + 1050 \text{ J})$ (C) $(U_1 - 150 \text{ J})$ (D) $(U_1 - 1050 \text{ J})$

Ans. (A)

16. The work done by a system is 8J when 40J heat is supplied to it. The change in internal energy of the system during the process :

- (A) 32 J (B) 40 J (C) 48 J (D) -32 J

Ans. (A)

17. Two moles of an ideal gas expand spontaneously into vacuum. The work done is :—

- (A) Zero (B) $2J$ (C) $4J$ (D) $8J$

Ans. (A)

18. The work done during the expansion of a gas from a volume of 4 dm^3 to 6 dm^3 against a constant external pressure of 3 atm is -

- (A) -608 J (B) $+304 \text{ J}$ (C) -304 J (D) -6 J

Ans. (A)

19. Assuming that water vapour is an ideal gas, the internal energy change (ΔU) when 1 mol of water is vapourised at 1 bar pressure and 100°C , (Given : Molar enthalpy of vapourisation of water at 1 bar and 373 K = 41 kJ mol^{-1} and $R = 8.3 \text{ J mol}^{-1} \text{ K}^{-1}$ will be) :- **[AIEEE-2007]**

- (A) 4.100 kJ mol⁻¹ (B) 3.7904 kJ mol⁻¹ (C) 37.904 kJ mol⁻¹ (D) 41.00 kJ mol⁻¹

Ans.(3)

20. A piston filled with 0.04 mol of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0°C. As it does so, it absorbs 208 J of heat. The values of q and w for the process will be :-

[JEE-MAIN-2013]

(R = 8.314 J/mol K) (ln 7.5 = 2.01)

(A) $q = + 208 \text{ J}$, $w = - 208 \text{ J}$

(B) $q = - 208 \text{ J}$, $w = - 208 \text{ J}$

(C) $q = - 208 \text{ J}$, $w = + 208 \text{ J}$

(D) $q = + 208 \text{ J}$, $w = + 208 \text{ J}$

Ans. (A)

Sol. $q = + 208 \text{ Joule}$

for isothermal process

$$\Delta U = 0$$

 \therefore from 1st law of thermodynamics

$$\Delta U = q + w$$

$$0 = q + w$$

$$\Rightarrow w = -q = -208 \text{ Joule}$$

9. CALCULATION OF q , w , ΔU & ΔH IN VARIOUS PROCESS :**9.1 ISOTHERMAL EXPANSION OR COMPRESSION OF IDEAL GAS :**For isothermal process : $\Delta T = 0$

$$\therefore \Delta U = n.C_{p,m}.\Delta T = 0$$

$$\Delta H = n.C_{p,m}.\Delta T = 0$$

and $q = \Delta U - w = -w$

Now, w depends on path (reversible or irreversible).**9.1.1 Reversible process :**

$$w_{\text{rev.}} = - \int_{V_1}^{V_2} P_{\text{ext}} \cdot dV = - \int_{V_1}^{V_2} (P \pm dP) \cdot dV = - \int_{V_1}^{V_2} P \cdot dV = - \int_{V_1}^{V_2} \frac{nRT}{V} \cdot dV$$

$$\therefore w_{\text{rev.}} = -nRT \cdot \ln \frac{V_2}{V_1} = -nRT \cdot \ln \frac{P_1}{P_2}$$

9.1.2 Irreversible process, against a constant external pressure :

$$w_{\text{irr.}} = -P_{\text{ext}} \int_{V_1}^{V_2} dV = -P_{\text{ext}}(V_2 - V_1)$$

9.1.3 Free expansion (or expansion in vacuum) :

$$P_{\text{ext}} = 0 \text{ but } dV = \text{finite, Hence, } w = 0$$

9.1.4 Comparison of magnitude of work :In expansion, magnitude of work = $-w_{\text{exp}}$ In compression, magnitude of work = w_{comp}

$$\text{Now, } w_{\text{rev}} - w_{\text{irr}} = (-P \cdot dV) - (-P_{\text{ext}} \cdot dV) = (P_{\text{ext}} - P) \cdot dV \\ = -ve, \text{ always}$$

In expansion, $P_{\text{ext}} < P$ and $dV = +ve$ In compression, $P_{\text{ext}} > P$ and $dV = -ve$

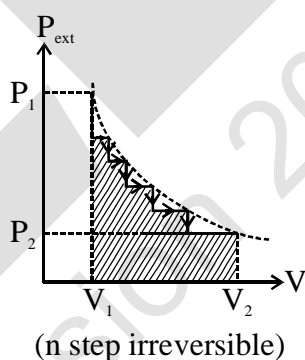
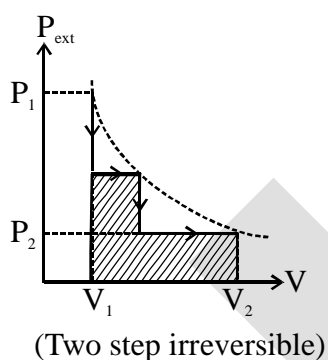
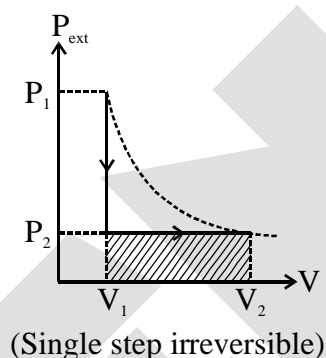
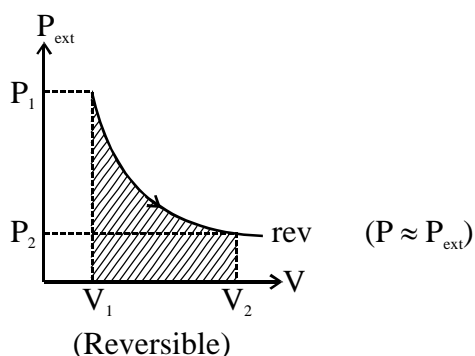
Hence, $w_{\text{rev}} < w_{\text{irr}}$ (Always, with proper sign).

Now, as magnitude of work in expansion is $-w_{\text{exp}}$, hence, $(-w_{\text{rev, exp}}) > (-w_{\text{irr, exp}})$, i.e., magnitude of work is greater when expansion is reversible.

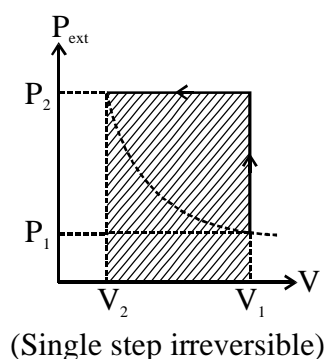
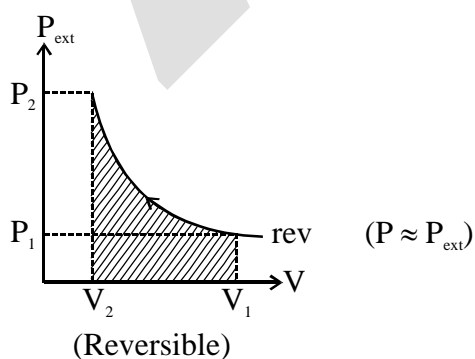
And, as magnitude of work in compression is w_{comp} , hence, $(w_{\text{rev, comp}}) < (w_{\text{irr, comp}})$, i.e., magnitude of work is greater when compression is irreversible.

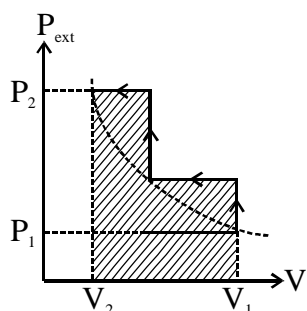
9.1.5 Graphical comparison :

(a) Expansion :

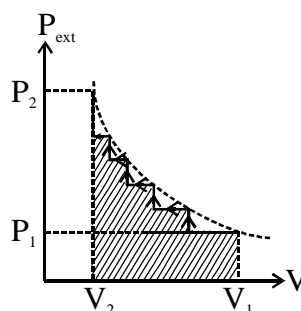

$$(-w_{\text{exp}}) : \text{Rev} > n \text{ step} > \dots > 2 \text{ step} > \text{single step}$$

(b) Compression :





(Two step irreversible)



(n step irreversible)

(w_{comp}) : Rev < n step < < 2 step < single step

Ex.1 Two moles of an ideal gas undergoes isothermal expansion from 4 L to 20 L at 27°C. Calculate q , w , ΔU and ΔH , if the process is performed.

- reversibly
- irreversibly, against a constant external pressure of 1 atm.
- as free expansion

Sol. For isothermal process, $\Delta T = 0$. Hence,

$$\Delta U = n \cdot C_{v,m} \cdot \Delta T = 0$$

$$\Delta H = n \cdot C_{p,m} \cdot \Delta T = 0$$

$$(i) \quad w = -nRT \cdot \ln \frac{V_2}{V_1} = -2 \times 8.314 \times 300 \times \ln \frac{20}{4} = -8028.52 \text{ J}$$

$$\text{and } q = -w = 8028.52 \text{ J}$$

$$(ii) \quad w = -P_{\text{ext}} \cdot (V_2 - V_1) = -1 \text{ atm} (20 \text{ L} - 4 \text{ L}) = -16 \text{ L-atm}$$

$$= -16 \times 101.3 \text{ J} = -1620.8 \text{ J}$$

$$q = -w = 1620.8 \text{ J}$$

$$(iii) \quad w = 0 \text{ and } q = 0$$

9.2 ADIABATIC EXPANSION OR COMPRESSION OF IDEAL GAS :

$$q = 0$$

$$\therefore \Delta U = w = n \cdot C_{v,m} \cdot (T_2 - T_1)$$

$$\text{and } \Delta H = n \cdot C_{p,m} \cdot (T_2 - T_1)$$

The change in temperature may be calculated as

$$n \cdot \int_{T_1}^{T_2} C_{v,m} \cdot dT = - \int_{V_1}^{V_2} P_{\text{ext}} \cdot dV$$

(a) If $C_{v,m}$ is temperature independent and the process is reversible, then

$$T \cdot V^{\gamma-1} = \text{constant}$$

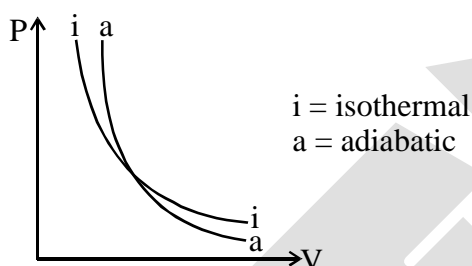
$$\text{or, } P \cdot V^{\gamma} = \text{constant}$$

$$\text{or, } T^{\gamma} P^{1-\gamma} = \text{constant}$$

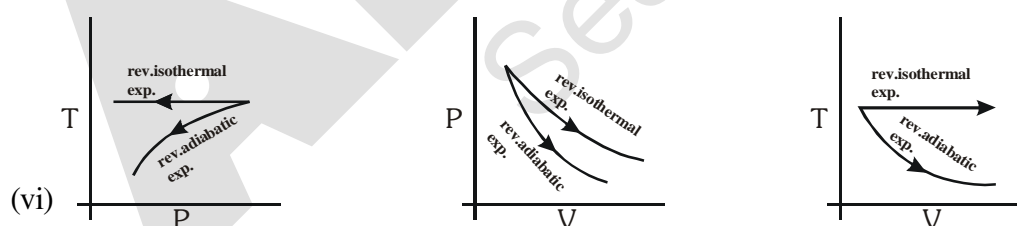
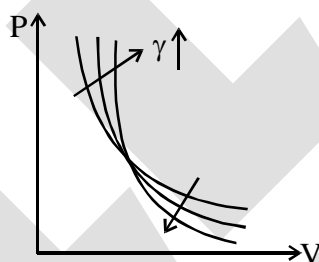
- (b) If $C_{v,m}$ is temperature independent and the process is irreversible, then

$$n.C_{v,m}.(T_2 - T_1) = -P_{ext}.(V_2 - V_1)$$

- (i) The temperature of ideal gas decreases in adiabatic expansion (except free expansion, which is isothermal too) and the temperature of ideal gas increases in adiabatic compression.
- (ii) The final temperature of gas is always higher in irreversible process (expansion or compression) relative to reversible process, for the same change in volume.
- (iii) Just like isothermal process, the magnitude of work is maximum when expansion is reversible and compression is irreversible (single step).
- (iv) Work in reversible isothermal and adiabatic processes may be compared graphically.



- (v) Work in reversible adiabatic process may be compared graphically.



Comparison of reversible adiabatic expansion and reversible isothermal expansion on TP, PV and TV diagram

Ex.2. Two moles of an ideal monoatomic gas undergoes adiabatic expansion from 5L, 127°C to 40L. Calculate q , ΔU , w and ΔH , if the process is performed.

- (i) reversibly
- (ii) irreversibly, against a constant external pressure of 0.1atm.
- (iii) as free expansion

Sol. : For adiabatic process, $q = 0$

$$(i) \quad T \cdot V^{\gamma-1} = \text{constant} \Rightarrow T_1 \cdot V_1^{\gamma-1} = T_2 \cdot V_2^{\gamma-1}$$

$$\therefore T_2 = T_1 \left(\frac{V_1}{V_2} \right)^{\gamma-1} = 400 \times \left(\frac{5}{40} \right)^{\frac{5}{3}-1} = 100\text{K}$$

$$\text{Now, } w = \Delta U = nC_v \Delta T = -7482.6 \text{ J}$$

$$\Delta H = \gamma \Delta U = -12471 \text{ J}$$

$$(ii) \quad \Delta U = w = -P_{\text{ext}} \cdot (V_2 - V_1) = -0.1 \times (40 - 5) \times 101.3 = -354.55 \text{ J}$$

$$\text{and } \Delta H = \frac{5}{3} \cdot \Delta U = -590.92 \text{ J}$$

$$(iii) \quad \Delta U = w = 0$$

$$\text{and } \Delta H = 0$$

Ex.3. Five moles of an ideal monoatomic gas undergoes adiabatic expansion from 12 atm to 1 atm, against a constant external pressure of 1 atm. If the initial temperature of gas is 27°C, calculate the final temperature. Also calculate q , ΔU , w and ΔH .

Sol. : $q = 0$

$$\Delta U = w$$

$$\text{or, } n \cdot C_{v,m} \cdot (T_2 - T_1) = -P_{\text{ext}} \cdot (V_2 - V_1)$$

$$\text{or, } n \cdot \frac{3}{2} R (T_2 - T_1) = -P_2 \left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right)$$

$$\text{or, } \frac{3}{2} (T_2 - 300) = - \left(T_2 - 300 \times \frac{1}{12} \right) \Rightarrow T_2 = 190\text{K}$$

$$\text{or, } \Delta U = w = 5 \times \frac{3}{2} R \times (190 - 300) = -6859.05 \text{ J}$$

$$\text{and } \Delta H = \gamma \cdot \Delta U = -11431.75 \text{ J}$$

9.3 ISOBARIC PROCESS FOR AN IDEAL GAS :

$$q = \Delta H = n \cdot C_{v,m} \cdot \Delta T$$

$$\therefore \Delta U = n \cdot C_{v,m} \cdot \Delta T$$

$$w = -P \cdot (V_2 - V_1) = -nR \cdot \Delta T$$

Ex.4. One mole of an ideal diatomic undergoes isobaric expansion from 27°C to 87°C . Calculate q , ΔU , w and ΔH .

Sol. : $q = \Delta H = n.C_{v,m}.\Delta T = 1 \times \frac{7}{2}R \times 60 = 1745.94 \text{ J}$

$$\Delta U = \frac{\Delta H}{\gamma} = 1247.1 \text{ J}$$

and $w = -nR.\Delta T = -1 \times 8.314 \times 60 = -498.84 \text{ J}$

9.4 ISOCHORIC PROCESS FOR AN IDEAL GAS :

$$w = 0$$

$$q = \Delta U = n.C_{v,m}.\Delta T$$

$$\therefore \Delta U = n.C_{v,m}.\Delta T$$

Ex.5. Ten moles of an ideal gas ($\gamma = 1.2$) is heated from 27°C to 47°C at constant volume. Calculate q , ΔU , w and ΔH .

Sol. : $w = 0$

$$q = \Delta U = n.C_{v,m}.\Delta T = 2 \times \frac{R}{1.2-1} \times 20 = 200 \text{ R}$$

$$\Delta H = \gamma.\Delta U = 240 \text{ R}$$

9.5 POLYTROPIC PROCESS FOR AN IDEAL GAS :

$$\Delta U = n.C_{v,m}.\Delta T$$

$$\therefore \Delta H = n.C_{p,m}.\Delta T$$

For ideal gas is reversible polytropic process and $C_{v,m}$ temperature independent,

$$P.V^x = \text{constant}$$

or, $T.V^{x-1} = \text{constant}$

where $x = \text{polytropic index}$

$$w_{\text{rev}} = \frac{P_2 V_2 - P_1 V_1}{1-x} = -\frac{nR(T_2 - T_1)}{1-x} \quad (x \neq 1)$$

$$= -nRT \cdot \ln \frac{V_2}{V_1} \quad (x = 1)$$

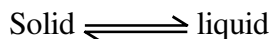
and $q = n.C_m.\Delta T$

The molar heat capacity, $C_m = C_{v,m} + \frac{P \cdot dV}{n \cdot dT} = C_{v,m} + \frac{R}{1-x}$

9.6 CYCLIC PROCESS :



9.7 CHANGE IN PHYSICAL STATE :



Changes in physical state occurs at constant pressure and temperature conditions.

$$\Delta U = q + w$$

$$q = \Delta H = m.L$$

$$\text{and } w = -P(V_{\text{final state}} - V_{\text{initial state}})$$

Ex.6. 90 gm water is completely converted into steam at 100°C and 1 atm. Calculate q , ΔU , w and ΔH . Latent heat of vaporisation of water at 100°C is 540 cal/gm.

Sol. : $\Delta H = m.L = 90 \times 540 = 48600 \text{ cal}$

$$w = -P(V_{\text{vap}} - V_{\text{water}}) = -P.V_{\text{vap}} = -nRT = -\frac{90}{18} \times 2 \times 373 = -3730 \text{ cal}$$

$$\Delta U = q + w = 48600 + (-3730) = 44870 \text{ cal}$$

EXERCISE # III

21. Find the work done when one mole of the gas is expanded reversibly and isothermally from 5 atm to 1 atm at 27°C. ($\ln 5 = 1.6$)

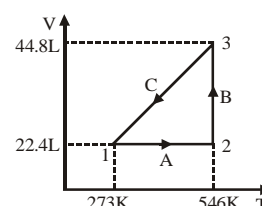
Ans. $w = -3.99 \text{ kJ}$

22. Five moles of an ideal gas at 300 K, expanded isothermally from an initial pressure of 4 atm to a final pressure of 1 atm against a constant external pressure of 1 atm. Calculate q , w , ΔU & ΔH . Calculate the corresponding value of all if the above process is carried out reversibly. ($\ln 2 = 0.7$)

Ans. $w_{\text{irr}} = -225 \text{ R}$, $w_{\text{rev}} = -210 \text{ R}$, $\Delta U = \Delta H = 0$, $q = -w$

23. One mole of an ideal monoatomic gas is carried through the reversible cycle of the given figure consisting of step A, B and C and involving state 1, 2 and 3. Fill in the blank space in the table given below assuming reversible steps.

Table-1			
State	P	V	T
1			
2			
3			



Step	Name of process	q	w	ΔU	ΔH
A					
B					
C					
overall					

Table-1

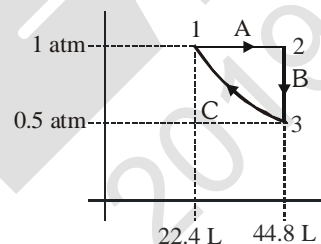
State	P	V	T
1	1 atm	22.4	273
2	2 atm	22.4	546
3	1 atm	44.8	546

Ans.

Step	Name of process	q	w	ΔE	ΔH
A	Isochoric	$3/2 R (273)$	0	$3/2 R (273)$	$5/2 R(273)$
B	Isothermal	$546 R \ln 2$	$-546 R \ln 2$	0	0
C	Isobaric	$-5/2 R(273)$	$R(273)$	$-3/2 R (273)$	$-5/2 R(273)$

- 24.** One mole of an ideal monoatomic gas is put through reversible path as shown in figure. Fill in the blank in the tables given below.

Table-1			
State	P	V	T
1			
2			
3			



Step	Name of process	q	w	ΔU	ΔH
A					
B					
C					
	cyclic				

Table-1

State	P	V	T
1	1 atm	22.4	273
2	1	44.8	546
3	0.5	44.8	273

Ans.

Step	Name of process	q	w	ΔE	ΔH
A	Isobaric	$5/2 R (273)$	$-R(273)$	$3/2 R (273)$	$5/2 R(273)$
B	Isochoric	$- 3/2 R (273)$	0	$- 3/2 R (273)$	$- 5/2 R (273)$
C	Isothermal	$- 273 R \ln 2$	$273 R \ln 2$	0	0
	Cyclic	$R(273) - 273 R \ln 2$	$-R(273)+ 273R \ln 2$	0	0

25. $\frac{1}{22.4}$ mol of an ideal monoatomic gas undergoes a reversible process for which $PV^2 = C$. The gas is expanded from initial volume of 1 L to final volume of 2 L starting from initial temperature of 273 K. Find the heat exchanged q during the process. Express your answer in litre atm.

$$R = \frac{22.4}{273} \text{ L atm mole}^{-1} \text{ degree}^{-1}.$$

Ans. -0.25

26. An ideal gas is allowed to expand both adiabatic reversibly and adiabatic irreversibly. If T_i is the initial temperature and T_f is the final temperature, which of the following statements is correct :-

[AIEEE-2006]

- (1) $T_f > T_i$ for reversible process but $T_f = T_i$ for irreversible process
- (2) $(T_f)_{\text{rev}} = (T_f)_{\text{irrev}}$
- (3) $T_f = T_i$ for both reversible and irreversible processes
- (4) $(T_f)_{\text{irrev}} > (T_f)_{\text{rev}}$

Ans. (4)

27. Which of the following statements/relationships is not correct in thermodynamic changes ?

- (1) $q = -nRT \ln \frac{V_2}{V_1}$ (isothermal reversible expansion of an ideal gas) [JEE-MAINS(online)-2014]
- (2) For a system at constant volume, heat involved merely changes to internal energy.
- (3) $w = -nRT \ln \frac{V_2}{V_1}$ (isothermal reversible expansion of an ideal gas)
- (4) $\Delta U = 0$ (isothermal reversible expansion of a gas)

Ans. (1)

10. SUMMARY

Process	Expression for w	Expression for q	ΔU	ΔH	Work on PV-graph
Reversible isothermal	$w = -nRT \ln \frac{V_2}{V_1}$ $= -nRT \ln \frac{P_1}{P_2}$	$q = nRT \ln \left(\frac{V_2}{V_1} \right)$ $q = nRT \ln \left(\frac{P_1}{P_2} \right)$	0 process	0	
Irreversible isothermal	$w = -P_{\text{ext}} (V_2 - V_1)$ $= -P_{\text{ext}} \left(\frac{nRT}{P_2} - \frac{nRT}{P_1} \right)$	$q = P_{\text{ext}} (V_2 - V_1)$	0	0	
Isobaric process	$w = -P_{\text{ext}} (V_2 - V_1)$ $= -nR\Delta T$	$q = \Delta H = nC_p \Delta T$	$\Delta U = nC_v \Delta T$	$\Delta H = nC_p \Delta T$	
Isochoric process	$w = 0$	$q = \Delta U = nC_v \Delta T$	$\Delta U = nC_v \Delta T$	$\Delta H = nC_p \Delta T$	
Reversible adiabatic process	$w = nC_v (T_2 - T_1)$ $= \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$	$q = 0$ $PV^\gamma = \text{constant}$ $TV^{\gamma-1} = \text{constant}$ $TP^{1-\gamma/\gamma} = \text{constant}$	$\Delta U = nC_v \Delta T$	$\Delta H = nC_p \Delta T$	
Irreversible adiabatic process	$w = nC_v (T_2 - T_1)$ $= \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$	$q = 0$ $nC_v (T_2 - T_1) =$ $-P_{\text{ext}} \left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right)$	$\Delta U = nC_v \Delta T$	$\Delta H = nC_p \Delta T$	
Polytropic	$w = \frac{P_2 V_2 - P_1 V_1}{n - 1}$ $w = \frac{R(T_2 - T_1)}{(n - 1)}$	$q = \int_{T_1}^{T_2} C_v dT$ $w = \frac{R(T_2 - T_1)}{(n - 1)}$	$\Delta U = nC_v \Delta T$	$\Delta H = nC_p \Delta T$	
Cyclic Process	Area enclosed in PV-diagram For clockwise -ive For anticlockwise +ive	$q = -w$	0	0	

11. LIMITATION OF FIRST LAW :

It can predict the change in energy as a result of change in state or vice-versa, but can not predict the natural direction of change (whether a change can happen on it's own or not).

MISCELLANEOUS PREVIOUS YEARS QUESTION

1. A sample of argon gas at 1 atm pressure and 27°C expands reversibly and adiabatically from 1.25 dm³ to 2.50 dm³. Calculate the enthalpy change in this process. $C_{v,m}$ for argon is 12.48 JK⁻¹ mol⁻¹. [JEE 2000]

Ans. $\Delta H \approx -115 \text{ J}$

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$$T_2 = T_1 \left(\frac{V_1}{V_2} \right)^{\gamma-1}$$

$$T_2 = 300 (1/2)^{8.3/12.48} \left[\gamma^{-1} \frac{R}{C_{v,m}} \right]$$

$$T_2 = 189.2 \text{ Kelvin.}$$

$$n = \frac{P_1 V_1}{RT_1} = \frac{(1)(1.25)}{(0.0821)(300)} = 0.507$$

$$\begin{aligned} \Delta H &= n C_{p,m} (T_2 - T_1) \\ &= 0.507 (20.78) (189.2 - 300) \\ &= -116.732 \text{ Joule.} \end{aligned}$$

2. Which of the following statement is false ?

[JEE 2001]

- (A) Work is a state function
(B) Temperature is a state function
(C) Change of state is completely defined when initial and final states are specified.
(D) Work appears at the boundary of the system

Ans. (A)

3. One mole of non-ideal gas undergoes a change of state (2.0 atm, 3.0 L, 95 K) to (4.0 atm, 5.0 L, 245 K) with a change in internal energy (ΔU) = 30.0 L-atm. The change in enthalpy (ΔH) of the process in L-atm.

[JEE 2002]

- (A) 40.0
(B) 42.3
(C) 44.0
(D) Not defined, because pressure is not constant

Ans. (C)

$$\Delta H = \Delta U + P_2 Y_2 - P_1 Y_1$$

$$\begin{aligned} \Delta H &= 30 + 20 - 6 \\ &= 44 \end{aligned}$$

4. One mole of a liquid (1 bar, 100 ml) is taken in an adiabatic container and the pressure increases steeply to 100 bar. Then at a constant pressure of 100 bar, volume decrease by 1 ml. Find ΔU and ΔH .

Ans. $\Delta U = 10 \text{ J}$, $\Delta H = 990 \text{ J}$

[JEE 2004]

$$0 + w = \Delta U$$

$$\Delta U = -P_{\text{ext}} (Y_2 - Y_1)$$

$$= -100 \left(\frac{-1}{1000} \right)$$

$$= 0.1 \text{ bar litre.}$$

$$\Delta H = \Delta U + P_2 Y_2 - P_1 Y_1$$

$$\Delta H = 0.1 + \left[\frac{100(99) - (1)(100)}{1000} \right]$$

$$\Delta H = 0.1 + 9.8$$

$$\Delta H = 9.9 \text{ bar. litre}$$

$$\Delta H = 990 \text{ Joules}$$

5. Two mole of an ideal gas is expanded isothermally and reversibly from 1 litre to 10 litre at 300 K. The enthalpy change (in KJ) for the process is :- **[JEE 2004]**
 (A) 11.4 kJ (B) - 11.4 kJ (C) 0 kJ (D) 4.8 kJ

Ans. (C)

In isothermal process $\Delta T = 0$

$$\Delta H = nC_{v,m} \Delta T$$

$$\Delta H = 0$$

6. One mole of monoatomic ideal gas expands adiabatically at initial temp. T against a constant external pressure of 1 atm from one litre to two litre. Find out the final temperature. ($R = 0.0821 \text{ litre. atm K}^{-1} \text{ mol}^{-1}$) **[JEE 2005]**

(A) T (B) $\frac{T}{(2)^{\frac{5}{3}-1}}$ (C) $T - \frac{2}{3 \times 0.0821}$ (D) $T + \frac{2}{3 \times 0.0821}$

Ans. (C)

$$-P_{\text{ext}} (V_2 - V_1) = nC_{v,m} (T_2 - T_1)$$

$$-1(2 - 1) = 1 \left(\frac{3}{2} R \right) (T_2 - T)$$

$$T_2 = T - \frac{2}{3R}$$

7. The molar heat capacity of a monoatomic gas for which the ratio of pressure and volume is one.

(A) $\frac{4}{2} R$ (B) $\frac{3}{2} R$ (C) $\frac{5}{2} R$ (D) zero **[JEE 2006]**

Ans. (A)

$$\frac{P}{V} = C$$

$$PV^{-1} = C$$

$$C_m = C_{v,m} + \frac{R}{1 - (-1)}$$

$$= \frac{3}{2} R + \frac{R}{2} = \frac{4R}{2}$$

8. Among the following, the state function(s) is (are) **[JEE 2009]**
 (A) Internal energy (B) Irreversible expansion work
 (C) Reversible expansion work (D) Molar enthalpy

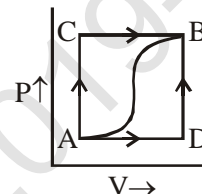
Ans. (A,D)

EXERCISE # S-I

BASIC

- Find the work done in each case :
 - When one mole of ideal gas in 10 litre container at 1 atm is allowed to enter an very large evacuated bulb of capacity 100 litre.
 - When 1 mole of gas expands from 1 litre to 5 litre against constant one atmospheric pressure.
 - Find the work done in atm-litre when 18 mL of water is getting vapourised at 373 K in open vessel. (*Assume the ideal behaviour of water vapour*).
 - Find total degree of freedom and break up as translational, rotational or vibrational degree of freedom in following cases.
 - CO_2
 - SO_2
 - He
 - NH_3
- ❑ **Problems related to First law of thermodynamics :**
- The gas is cooled such that it loses 65 J of heat. The gas contracts as it cools and work done on the system is equal to 20 J. What are q , w and ΔU ?
 - When a system is taken from state A to state B along the path ACB, 80J of heat flows into the system and the system does 30J of work.
 - How much heat flows into the system along path ADB if the work done by the system is 10J ?
 - When the system is returned from state B to A along the curved path, the work done on the system is 20J. Does the system absorb or liberate heat, and how much ?
 - If $U_D - U_A = 40\text{J}$, find the heat absorbed in the process AD and DB if work done by system in ADB is 10 Joule.
 - An ideal gas undergoes expansion from A(10 atm, 1 litre) to B(1 atm, 10 litre), first against 5 atm and then against 1 atm, isothermally. Calculate the amount of heat absorbed (in litre. atm)
 - 2 moles of an ideal gas is compressed from (1 bar, 2L) to 2 bar isothermally. Calculate magnitude of minimum possible work involved in the change (in Joules). (Given : 1 bar L = 100 J) ($\ln 2 = 0.7$)
 - 2 mole of an ideal gas undergoes isothermal compression along three different paths if it's initial state is (2 bar, 4 litre) in all three process.
 - Reversible compression from till 20 bar.
 - A single stage compression against a constant external pressure of 20 bar
 - A two stage compression consisting initially of compression against a constant external pressure of 10 bar until $P_{\text{gas}} = P_{\text{ext}}$, followed by compression against a constant pressure of 20 bar until $P_{\text{gas}} = P_{\text{ext}}$.

Calculate the work (in bar. L) for each of these processes and for which of the irreversible processes is the magnitude of the work greater ? [Given : $R = 0.08 \text{ bar. L/mole.K}$]
 - A monoatomic ideal gas undergoing irreversible adiabatic compression from 4L to 1L against 1 bar pressure. Calculate the enthalpy change of gas. [Given : 1 bar-L = 100 J]
 - Two mole of ideal diatomic gas ($C_{V,m} = 5/2 R$) at 300K and 5 atm expanded irreversibly & adiabatically to a final pressure of 2 atm against a constant pressure of 1 atm. Calculate q , w , ΔH & ΔU .



11. Calculate the work done by system in an irreversible (single step) adiabatic expansion of 1 mole of a polyatomic gas ($\gamma = 4/3$) from 400 K and pressure 10 atm to 1 atm.
12. 1 mole of CO_2 gas at 300 K is expanded under reversible adiabatic condition such that its volume becomes 27 times.

(a) What is the final temperature ?

(b) What is work done ?

Given $\gamma = 1.33$ and $C_V = 25.08 \text{ J mol}^{-1} \text{ K}^{-1}$ for CO_2 .

13. Molar heat capacity of an ideal gas at constant volume is given by $C_V = (16.5 + 10^{-2}T) \frac{\text{J}}{\text{K} - \text{mol}}$. If 2 moles of this ideal gas are heated at constant volume from 300K to 400K. Then the change in internal energy (in kJ) will be approximately.
14. Three moles of an ideal gas at 200 K and 2.0 atm pressure undergoes reversible adiabatic compression until the temperature becomes 250 K. For the gas C_V is $27.5 \text{ JK}^{-1} \text{ mol}^{-1}$ in this temperature range. Calculate q , w , ΔU , ΔH and final V and final P .

$$\text{Given } \left(\frac{5}{4}\right)^{1/0.3} = 2.1, \left(\frac{5}{4}\right)^{35.8/8.3} = 2.61$$

[$R = 8.3 \text{ Joule/mol.K}$ or $R = 0.0821 \text{ atm litre/mol.K}$]

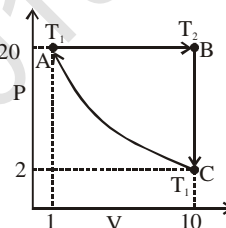
❑ Problem related to cyclic process

15. One mole of a perfect monoatomic gas is put through a cycle consisting of the following three reversible steps :

(CA) Isothermal compression from 2 atm and 10 litres to 20 atm and 1 litre.

(AB) Isobaric expansion to return the gas to the original volume of 10 litres with

T going from T_1 to T_2 . (BC) Cooling at constant volume to bring the gas to the original pressure and temperature. The steps are shown schematically in the figure shown.



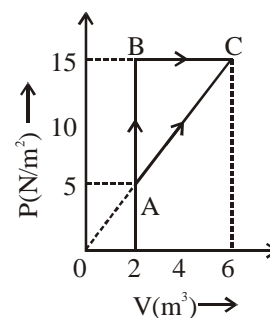
(a) Calculate T_1 and T_2

(b) Calculate ΔU , q and w (in calories) for the cycle.

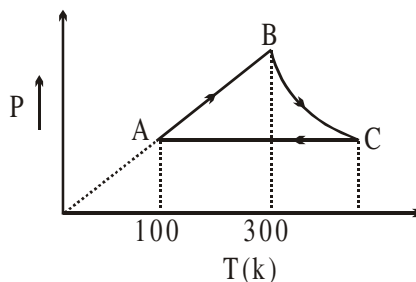
[Given : $\ln 10 = 2.3$, $R = 0.821 \text{ atm.litre/mol.K}$ or $R = 2 \text{ cal/mol.K}$]

16. The given figure shows a change of state A to state C by two paths ABC and AC for an ideal gas. Calculate the :

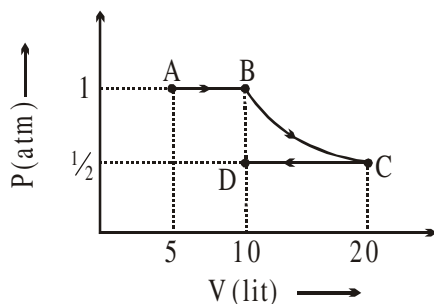
- (a) Path along which magnitude of work done is least ABC or AC
- (b) Internal energy at C if the internal energy of gas at A is 10 J and amount of heat supplied to change its state to C through the path AC is 200J.
- (c) Amount of heat supplied to the gas to go from A to B, if internal energy change of gas from A to B is 10 J.



17. Calculate the net work done in the following cycle for one mol of an ideal gas (in calorie), where in process BC, $PT = \text{constant}$. ($R = 2 \text{ cal/mol-K}$).



18.



Calculate magnitude of total work done (in atm.lit) for the above process ABCD involving a monoatomic ideal gas. [Given : $\ln 2 = 0.7$]

❑ **Problem based on polytropic process**

19. For 1 mole of ideal monoatomic gas if $\frac{P}{V^2} = \text{constant}$ and initial temperature is 100 K. If gas is expanded from 1 L to 2 L then find (a) heat capacity (b) total heat absorbed (c) work (d) change in internal energy.

(Assume $R = 0.0821 \frac{\text{L-atm}}{\text{mole-K}}$, $1 \text{ L-atm} = 24 \text{ cal}$)

20. One mole of an ideal monoatomic gas undergoes expansion along a straight line on P-V curve from initial state A(3L, 8 atm) to final state B(7.5 L, 2 atm). Calculate q for the above process in L atm.

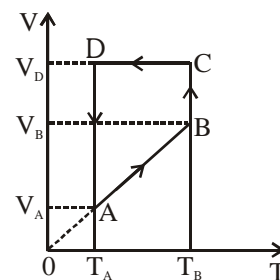
❑ **Problems based on change in physical state :**

21. Water expands when it freezes. Determine amount of work done, in joules, when a system consisting of 1.0 L of liquid water freezes under a constant pressure of 1.0 atm and forms 1.1 L of ice.
22. What is ΔU when 2.0 mole of liquid water vaporises at 100°C ? The heat of vaporisation, ΔH_{vapour} of water at 100°C is $40.66 \text{ kJ mol}^{-1}$.
23. When 1 mole of ice melt at 0°C and at constant pressure of 1 atm, 1440 calories of heat are absorbed by the system. The molar volumes of ice and water are 0.0196 and 0.0180 litre respectively. Calculate ΔH and ΔU for the reaction.

EXERCISE # S-II

1. A monoatomic ideal gas of two moles is taken through a reversible cyclic process starting from A as shown in figure. The volume ratios

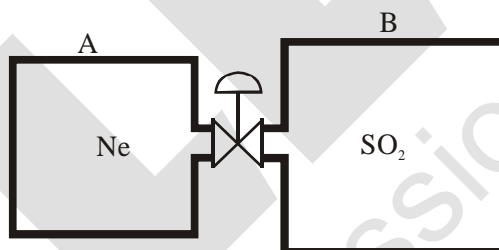
are $\frac{V_B}{V_A} = 2$ and $\frac{V_D}{V_A} = 4$. If the temperature T_A at A is 27°C , calculate:



- The temperature of the gas at point B.
 - Heat absorbed or released by the gas in each process.
 - The total work done by the gas during complete cycle. ($\ln 2 = 0.7$)
2. One mole of an ideal gas (not necessarily monoatomic) is subjected to the following sequence of steps.
- It is heated at constant volume from 298 K to 373 K
 - It is expanded freely into a vacuum to double volume at 373 K.
 - It is cooled reversibly at constant pressure to 298K.
- Calculate q , w , ΔU and ΔH for the overall process.
3. Derive a mathematical expression for the work done when n -mole a gas that has the equation of state $PV = nRT - \frac{n^2a}{V}$ expands reversibly from V_i to V_f at constant temperature T .
4. 3 dm^3 of an ideal monoatomic gas at 600 K and 32 bar expands until pressure of the gas is 1 bar Calculate q , w , ΔU and ΔH for the process if the expansion is :
- (Use : $R = 0.08 \text{ bar litre/mol-K}$, $= 2 \text{ cal / mol-K}$)
- Isothermal and reversible
 - Adiabatic and reversible
 - Isothermal and adiabatic
 - Against 1 bar and adiabatic
 - Against 1 bar and isothermal.
5. Pressure over 1000 mL of a liquid is gradually increased from 1 bar to 1001 bar under adiabatic conditions. If the final volume of the liquid is 990 mL, calculate ΔU and ΔH of the process, assuming linear variation of volume with pressure.
6. At 500 kilobar pressure, density of diamond and graphite are 3 g/cc and 2 g/cc respectively, at certain temperature 'T'. Find the value $|\Delta H - \Delta U|$ (kJ/mole) for the conversion of 1 mole of graphite to 1 mole of diamond at temperature 'T' :
7. 2 mole of ideal monoatomic gas was subjected to reversible adiabatic compression from initial state of $P = 1 \text{ atm}$ and $T = 300 \text{ K}$ till the pressure is $4\sqrt{2} \text{ atm}$ and temperature is TK . The gas is then subjected to reversible isothermal expansion at TK till the internal pressure is one atm. The gas is now isobarically cooled to attain initial state. Find W_{Net} (in calorie) for whole process.

[Use $\ln 2 = 0.7$, $R = 2 \text{ cal/K-mol}$]

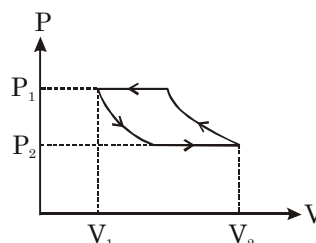
8. One mole of an ideal gas at 300 K is heated at constant volume (V_1) until its temperature is doubled, then it is subjected to isothermal reversible expansion till it reaches the original pressure. Finally the gas is cooled at constant pressure till system reached to the half of original volume ($V_1/2$). Determine total work done ($|w|$) in cal. [Use : $\ln 2 = 0.70$; $R = 2 \text{ Cal/K.mol.}$]
9. How many times volume of diatomic gas should be expanded reversibly & adiabatically in order to reduce its r.m.s velocity to half.
10. 0.5 mole each of two ideal gases A ($C_v = \frac{3}{2}R$) and B ($C_v = \frac{5}{2}R$) are taken in a container and expanded reversibly and adiabatically from $V = 1 \text{ L}$ to $V = 4 \text{ L}$ starting from initial temperature $T = 300 \text{ K}$. Find $|\Delta H|$ for the process in (cal/mol).
11. 0.50 mol of an ideal gas initially at a temperature of 300 K and at a pressure of 2 atm is expanded isothermally in three steps. In each step, the pressure is dropped suddenly and held constant until equilibrium is re-established. The pressure at each of the three stages of expansion are 1.6, 1.2 and 1 atm. Calculate the work done ($|W|$) (in atm-litre) in this process.
[Use $R = 0.08 \text{ atm litre/ mole. K}$]
12. Two rigid adiabatic vessels A and B which initially, contains two gases at different temperatures are connected by pipe line with valve of negligible volume. The vessel 'A' contains 2 moles Ne gas ($C_{p,m} = \frac{5}{2}R$) at 300 K, vessel 'B' contains 3 moles of SO_2 gas ($C_{p,m} = 4R$) at 400 K. The volume of A & B vessel is 4 and 6 litre respectively. The final total pressure (in atm) when valve is opened and 12 Kcal heat supplied through it to vessels.
[Use : $R = 2 \text{ cal/mol. K}$ and $R = 0.08 \text{ L. atm / mol K}$ as per desire]



13. One mole of an ideal monoatomic gas initially at 1200 K and 64 atm is expanded to a final state at 300 K and 1.00 atm. To achieve change, a reversible path is constructed that involve an adiabatic expansion in the beginning followed by an isothermal expansion to the final state. Determine the magnitude of net work done by the gas, in cal. ($R = 2 \text{ cal/K-mol. } \ln 2 = 0.7$)
14. An ideal gas is carried through a thermodynamic cycle.

$$P_1 = 10 \text{ bar} \quad V_1 = \frac{1}{\ln 10} \text{ litre}$$

$$P_2 = 1 \text{ bar} \quad V_2 = \frac{4}{\ln 10} \text{ litre}$$



Consisting of two isobaric and two isothermal processes. Calculate the net work in the entire cycle in litre bar.

EXERCISE # O-I

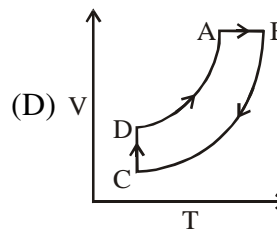
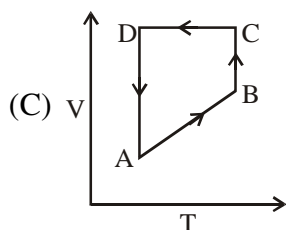
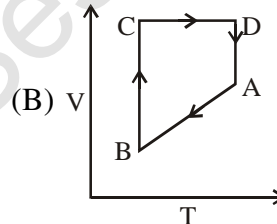
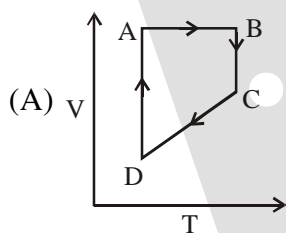
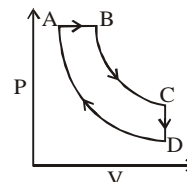
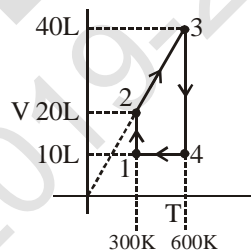
BASIC

- Out of boiling point (I), entropy (II), pH (III) and density (IV), intensive properties are
(A) I, II (B) I, II, III (C) I, III, IV (D) All of these
- What is the change in internal energy when a gas is compressed from 377 ml to 177 ml under a constant pressure of 1520 torr, while at the same time being cooled by removing 124 J heat ?
[Take : (1L atm) = 100 J]
(A) -24 J (B) - 84 J (C) - 164 J (D) - 248 J
- One mole of an ideal monoatomic gas expanded irreversibly in two stage expansion.
State-1 (8.0 bar, 4.0 litre, 300 K)
State-2 (2.0 bar, 16litre, 300 K)
State-3 (1.0 bar, 32 litre, 300 K)
Total heat absorbed by the gas in the process is :
(A) 116J (B) 40 J (C) 4000 J (D) None of these
- An ideal gas undergoes isothermal expansion from A(10 atm, 1l) to B(1 atm, 10 l) either by
(I) Infinite stage expansion or by
(II) First against 5 atm and then against 1 atm isothermally
Calculate $\frac{q_I}{q_{II}}$:
(A) $\frac{1}{13 \times 2.303}$ (B) 13×2.303 (C) $\frac{13}{23.03}$ (D) $\frac{23.03}{13}$
- One mole of ideal gas is allowed to expand reversibly and adiabatically from a temperature of 27°C. If the work done by the gas in the process is 3 kJ, the final temperature will be equal to -
($C_v = 20 \text{ J/K mol}$)
(A) 100 K (B) 450 K (C) 150 K (D) 400 K
- For an adiabatic process, which of the following relation must be correct -
(A) $\Delta U = 0$ (B) $P \Delta V = 0$ (C) $q = 0$ (D) $q = + W$
- A system containing ideal gas is expanded under adiabatic process
(A) Temperature increases (B) Internal energy decreases
(C) Internal energy increases (D) None of these
- A gas $\left(C_{v,m} = \frac{5}{2} R\right)$ behaving ideally was allowed to expand reversibly and adiabatically from 1 litre to 32 litre. It's initial temperature was 327° C. The molar enthalpy change (in J/mole) for the process is :-
(A) -1125 R (B) - 575 R (C) -1575 R (D) None of these
- Two moles of an ideal gas ($C_v = \frac{5}{2} R$) was compressed adiabatically against constant pressure of 2 atm, which was initially at 350 K and 1 atm pressure. The work involve in the process is equal to -
(A) 250 R (B) 300 R (C) 400 R (D) 500 R

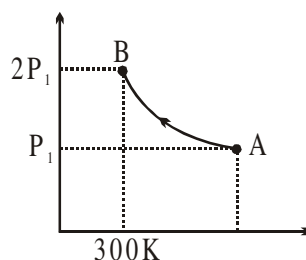
10. A gas is expanded from volume V_1 to V_2 through three different process :
 (a) Reversible adiabatic (b) Reversible isothermal (c) Irreversible adiabatic

The correct statements is -

- (A) $(T_f)_{\text{Reversible Isothermal}} > (T_f)_{\text{Reversible adiabatic}} > (T_f)_{\text{Irreversible adiabatic}}$
 (B) $(T_f)_{\text{Reversible Isothermal}} > (T_f)_{\text{Irreversible adiabatic}} > (T_f)_{\text{Reversible adiabatic}}$
 (C) $W_{\text{Reversible Isothermal}} > W_{\text{Irreversible adiabatic}} > W_{\text{reversible adiabatic}}$
 (D) $(P_f)_{\text{Reversible Isothermal}} > (P_f)_{\text{Reversible adiabatic}} > (P_f)_{\text{Irreversible adiabatic}}$
11. What is the magnitude of work performed by one mole of an ideal gas when its volume increases eight times in irreversible adiabatic expansion if the initial temperature of the gas is 300 K ? C_v for the gas is $1.5 R$. ($R = 2 \text{ Cal / mol / K}$)
 (A) 900 Cal (B) 450 Cal (C) 675 Cal (D) 331.57 Cal
12. For a process which follows the equation $PV^3 = C$, the work done when one mole of ideal gas was taken from 1 atm to $2\sqrt{2}$ atm starting from initial temperature of 300 K is
 (A) 300 R (B) 150 R (C) 600 R (D) 900 R
13. What is the net work done (w) when 1 mole of monoatomic ideal gas undergoes in a process described by 1, 2, 3, 4 in given V - T graph
 Use : $R = 2 \text{ cal/mole K}$
 $\ln 2 = 0.7$
 (A) -600 cal (B) - 660 cal
 (C) + 660 cal (D) + 600 cal
14. A cyclic process ABCD is shown in PV diagram for an ideal gas.
 which of the following diagram represents the same process ?

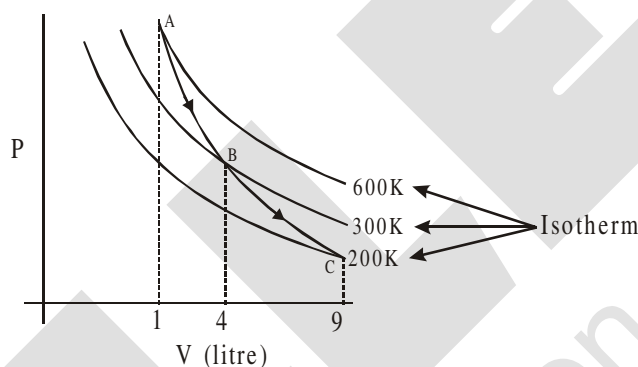


15. 2 moles of an ideal monoatomic gas is taken from state A to state B through a process AB in which $PT = \text{constant}$. The process can be represented on a P-T graph as follows:

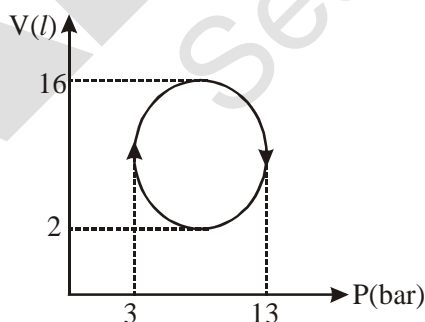


Select the incorrect option(s):

- (A) Heat evolved by the gas during process AB = $2100 R$
 (B) Heat absorbed by the gas during process AB = $2100 R$
 (C) $\Delta U = -900 R$
 (D) $W = 1200R$
16. The given figure shows a polytropic process ABC for one mole of an ideal gas. Calculate the polytropic index (x) for the process-

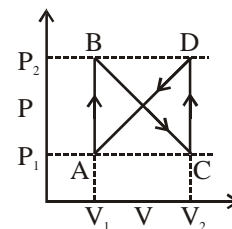


- (A) $1/2$ (B) $-1/2$ (C) $3/2$ (D) None
17. Work in the following cyclic process is



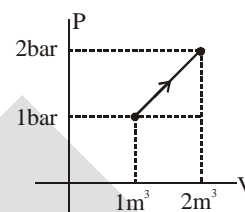
- (A) -11 (B) -11000 (C) 11 (D) 11000

18. An ideal gas is taken around the cycle ABCDA as shown in figure. The net work done during the cycle is equal to :-



- (A) Zero
(B) Positive
(C) Negative
(D) We cannot predict

19. What is ΔU for the process described by figure. Heat supplied during the process $q = 200$ kJ.



- (A) +50 kJ
(B) -50 kJ
(C) -150 kJ
(D) +150 kJ

20. A diatomic ideal gas initially at 273 K is given 100 cal heat due to which system did 209 J work, Molar heat capacity (C_m) of gas for the process is [1 cal = 4.18 Joule]

- (A) $\frac{3}{2}R$ (B) $\frac{5}{2}R$ (C) $\frac{5}{4}R$ (D) $5R$

21. For an ideal monoatomic gas during any process $T = kV$, find out the molar heat capacity of the gas during the process. (Assume vibrational degree of freedom to be active)

- (A) $\frac{5}{2}R$ (B) $3R$ (C) $\frac{7}{2}R$ (D) $4R$

22. An amount Q of heat is added to a monoatomic ideal gas in a process in which the gas performs a work $Q/2$ on its surrounding. The molar heat capacity of gas (in cal/K-mol) for the process is.

- (A) $3R$ (B) $5R$ (C) $4R$ (D) $2R$

EXERCISE # O-II

❑ ONE OR MORE THAN ONE MAY BE CORRECT :

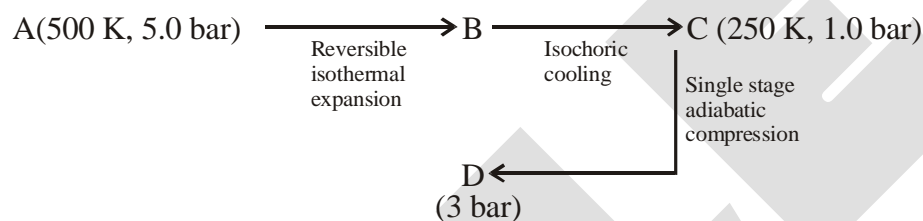
1. An insulated container of gas has two chambers separated by an insulating partition. One of the chambers has volume V_1 and contains ideal gas at pressure P_1 and temperature T_1 . The other chamber has volume V_2 and contains same ideal gas at pressure P_2 and temperature T_2 . If the partition is removed without doing any work on the gas, the final equilibrium temperature of the gas in the container will be :-

(A) $\frac{T_1 T_2 (P_1 V_1 + P_2 V_2)}{P_1 V_1 T_2 + P_2 V_2 T_1}$ (B) $\frac{P_1 V_1 T_1 + P_2 V_2 T_2}{P_1 V_1 + P_2 V_2}$ (C) $\frac{P_1 V_1 T_2 + P_2 V_2 T_1}{P_1 V_1 + P_2 V_2}$ (D) $\frac{T_1 T_2 (P_1 V_1 + P_2 V_2)}{P_1 V_1 T_1 + P_2 V_2 T_2}$

2. The heat capacity of liquid water is 75.6 J/mol.K, while the enthalpy of fusion of ice is 6.0 kJ/mol. What is the smallest number of ice cubes at 0°C, each containing 9.0 g of water, needed to cool 500 g of liquid water from 20°C to 0°C ?

(A) 1 (B) 7 (C) 14 (D) 252

3. Two moles of an ideal gas ($C_{v,m} = \frac{3}{2}R$) is subjected to following change of state



The correct statement is/are

(A) The pressure at B is 2.0 bar (B) The temperature at D is 450 K
(C) $\Delta H_{CD} = 1000 R$ (D) $\Delta U_{BC} = 375 R$

4. A real gas is subjected to an adiabatic process from (2 bar, 40 lit., 300 K) to (4 bar, 30 lit., 300 K) against a constant pressure 4 bar the enthalpy change for the process is

(A) Zero (B) 6000 J (C) 8000 J (D) 80 J

5. Which of the following statement is/are correct ?

- (A) Enthalpy can be written as $H = f(V, T)$ for a substance (no physical or chemical change)
(B) Absolute value of enthalpy can not be determined
(C) The heat absorbed during the isothermal expansion of an ideal gas against vacuum is zero
(D) During compression of an ideal gas at constant pressure the temperature of gas decreases.

6. Choose the correct statement(s) :-

- (A) During adiabatic expansion of an ideal gas, magnitude of work obtained is equal to ΔH of gas.
(B) For same change in temperature of ideal gas through adiabatic process, magnitude of W will be same in reversible as well as irreversible process.
(C) During an adiabatic reversible expansion of an ideal gas, temperature of the system increases.
(D) For same change in volume of ideal gas, ΔU is less in adiabatic expansion than in isobaric expansion if expansion starts with same initial state.

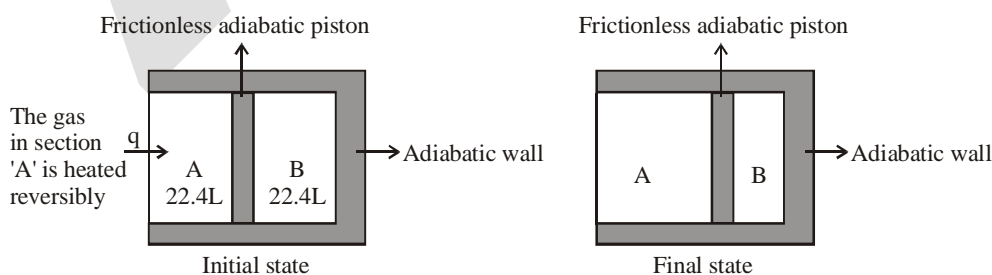
7. Choose the correct statement(s) among the following :-
- (A) Internal energy of H_2O remains constant during conversion of liquid into its vapour at constant temperature.
- (B) During fusion of ice into water, enthalpy change and internal energy change are almost same at constant temperature.
- (C) Molar heat capacity of gases are temperature dependent
- (D) During boiling of H_2O at 1 atm, $100^\circ C$, average kinetic energy of H_2O molecules increases.
8. Suppose that the volume of a certain ideal gas is to be doubled by one of the following processes :
- (A) isothermal expansion (B) adiabatic expansion
- (C) free expansion in insulated condition (D) expansion at constant pressure.
- If E_1, E_2, E_3 and E_4 respectively are the changes in average kinetic energy of the molecules for the above four processes, then-
- (A) $E_2 = E_3$ (B) $E_1 = E_3$ (C) $E_1 > E_4$ (D) $E_4 > E_3$

❑ **Assertion / reason :**

9. **Statement-1 :** There is no change in enthalpy of an ideal gas during compression at constant temperature.
- Statement-2 :** Enthalpy of an ideal gas is a function of temperature and pressure.
- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
- (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
- (C) Statement-1 is true, statement-2 is false.
- (D) Statement-1 is false, statement-2 is true.
10. **Statement-1 :** Due to adiabatic expansion, the temperature of an ideal gas always decreases.
- Statement-2 :** For an adiabatic process, $\Delta U = w$.
- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
- (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
- (C) Statement-1 is true, statement-2 is false.
- (D) Statement-1 is false, statement-2 is true.

Paragraph for Q.11 to Q.13

A cylindrical container of volume 44.8 litres is containing equal no. of moles (in integer no.) of an ideal monoatomic gas in two sections A and B separated by an adiabatic frictionless piston as shown in figure. The initial temperature and pressure of gas in both section is $27.3K$ and 1 atm. Now gas in section 'A' is slowly heated till the volume of section B becomes $(1/8)^{th}$ of initial volume.



Given : $R = 2 \text{ cal/mol-K}$, $C_{v,m}$ of monoatomic gas $= \frac{3}{2} R$,

At 1 atm & $0^\circ C$ ideal gas occupy 22.4 litre.

11. What will be the final pressure in container B.
 (A) 2 atm (B) 8 atm (C) 16 atm (D) 32 atm
12. Final temperature in container A will be
 (A) 1638 K (B) 6988 K (C) 3274 K (D) 51 K
13. Change in enthalpy for section A in Kcal
 (A) 48.3 (B) 80.53 (C) 4.83 (D) 8.05

Paragraph for Q.14 to 16

As a result of the isobaric heating by $\Delta T = 72\text{K}$, one mole of a certain ideal gas obtains an amount of heat $Q = 1.60\text{ kJ}$.

14. The work performed by the gas is -
 (A) 8.60 kJ (B) 0.60 kJ (C) 16.60 kJ (D) 4.60 kJ
15. The increment of its internal energy (in kJ) is -
 (A) 1.0 (B) 1.6 (C) 2.2 (D) 2.0
16. The value of γ for the gas is -
 (A) 0.6 (B) 1.4 (C) 1.6 (D) 1.5

MATCH THE COLUMN :

17. Match Column-I with Column-II

Column-I (Ideal Gas)

- (A) Reversible isothermal process
 (B) Reversible adiabatic process
 (C) Irreversible adiabatic process
 (D) Irreversible isothermal process

Column-II (Related equations)

- (P) $W = 2.303 n RT \log(P_2/P_1)$
 (Q) $W = nC_{V,m} (T_2 - T_1)$
 (R) $W = -2.303nRT \log(V_2/V_1)$
 (S) $W = -\int_{V_i}^{V_f} P_{\text{ext.}} dV$

18. Match the column

Column-I

- (A) Isothermal vaporisation of water at 100°C & 1 atm
 (B) Isothermal reversible expansion of an ideal gas
 (C) Adiabatic free expansion of ideal gas
 (D) Isochoric heating of an ideal gas

Column-II

- (P) $\Delta T = 0$
 (Q) $\Delta U = 0$
 (R) $\Delta H = 0$
 (S) $q = 0$
 (T) $w = 0$

MATCH THE LIST :

19. Match the following, and select the correct code :-

Column-I

- (P) Isothermal process (reversible)
 (Q) Adiabatic process (reversible)
 (R) Isochoric process
 (S) Isothermal process (irreversible)

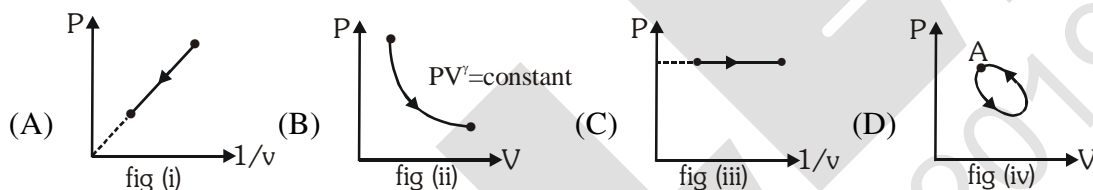
Column-II

- (1) $q = 2.303 nRT \log \frac{P_1}{P_2}$
 (2) $PV^\gamma = \text{const.}$
 (3) $q = P_{\text{ext.}} (V_2 - V_1)$
 (4) Area under P-V curve is zero

Code:

	P	Q	R	S
(A)	2	1	4	3
(B)	1	2	4	3
(C)	2	1	3	4
(D)	1	2	3	4

20. The figures given below depict different processes for a given amount of an ideal gas.



Column-I

- (P) In Fig (i)
 (Q) In Fig (ii)
 (R) In Fig (iii)
 (S) In Fig (iv)

Column-II

- (1) Net heat is absorbed by the system
 (2) Net work is done on the system
 (3) Net heat is rejected by the system
 (4) Net work is done by the system
 (5) Net internal energy remains constant

Code:

	P	Q	R	S
(A)	1, 4, 5	4	2, 3	2, 3, 5
(B)	1, 4, 5	4	2, 3	2, 3
(C)	1, 2, 4	2	1, 4	2, 3
(D)	1, 2	2	1, 4	3, 5

EXERCISE # J-MAIN

- A piston filled with 0.04 mol of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0°C. As it does so, it absorbs 208 J of heat. The values of q and w for the process will be :- **[Jee-Main-2013]**

($R = 8.314 \text{ J/mol K}$) ($\ln 7.5 = 2.01$)

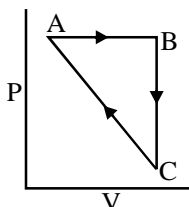
 - $q = + 208 \text{ J}$, $w = - 208 \text{ J}$
 - $q = - 208 \text{ J}$, $w = - 208 \text{ J}$
 - $q = - 208 \text{ J}$, $w = + 208 \text{ J}$
 - $q = + 208 \text{ J}$, $w = + 208 \text{ J}$
- Which of the following statements/relationships is not correct in thermodynamic changes ?

 - $q = -nRT \ln \frac{V_2}{V_1}$ (isothermal reversible expansion of an ideal gas) **[Jee-Main_(Online)-2014]**
 - For a system at constant volume, heat involved merely changes to internal energy.
 - $w = -nRT \ln \frac{V_2}{V_1}$ (isothermal reversible expansion of an ideal gas)
 - $\Delta U = 0$ (isothermal reversible expansion of a gas)
- A gas undergoes change from state A to state B. In this process, the heat absorbed and work done by the gas is 5 J and 8 J, respectively. Now gas is brought back to A by another process during which 3 J of heat is evolved. In this reverse process of B to A:- **[Jee-Main_(Online)-2017]**

 - 10 J of the work will be done by the surrounding on gas.
 - 6 J of the work will be done by the surrounding on gas.
 - 10 J of the work will be done by the gas.
 - 6 J of the work will be done by the gas.
- The enthalpy change on freezing of 1 mol of water at 5°C to ice at -5°C is: **[Jee-Main_(Online)-2017]**
(Given $\Delta_{\text{fus}}H = 6 \text{ kJ mol}^{-1}$ at 0°C, $C_p(\text{H}_2\text{O}, l) = 75.3 \text{ J mol}^{-1} \text{ K}^{-1}$, $C_p(\text{H}_2\text{O}, s) = 36.8 \text{ J mol}^{-1} \text{ K}^{-1}$)

 - 6.56 kJ mol⁻¹
 - 5.81 kJ mol⁻¹
 - 6.00 kJ mol⁻¹
 - 5.44 kJ mol⁻¹
- ΔU is equal to **[Jee-Main_(Online)-2017]**

 - Isochoric work
 - Isobaric work
 - Adiabatic work
 - Isothermal work
- An ideal gas undergoes a cyclic process as shown in figure. **[Jee-Main_(Online)-2018]**



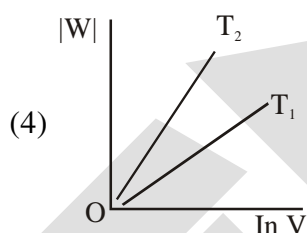
$$\Delta U_{BC} = -5 \text{ kJ mol}^{-1}, q_{AB} = 2 \text{ kJ mol}^{-1}$$

$$W_{AB} = -5 \text{ kJ mol}^{-1}, W_{CA} = 3 \text{ kJ mol}^{-1}$$

Heat absorbed by the system during process CA is :-

- (1) 18 kJ mol^{-1} (2) $+5 \text{ kJ mol}^{-1}$ (3) -5 kJ mol^{-1} (4) -18 kJ mol^{-1}

- [Jee-Main_(Online)-2019]**

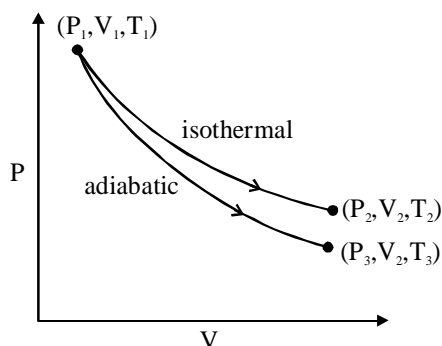


- [JEE-MAINS(online)-2019]**

- (1) $\frac{3}{2}$ K (2) $\frac{2}{3}$ K (3) 1 K (4) 2 K

EXERCISE # J-ADVANCED

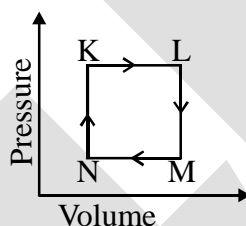
1. The reversible expansion of an ideal gas under adiabatic and isothermal conditions is shown in the figure. Which of the following statement(s) is (are) correct ? [JEE 2012]



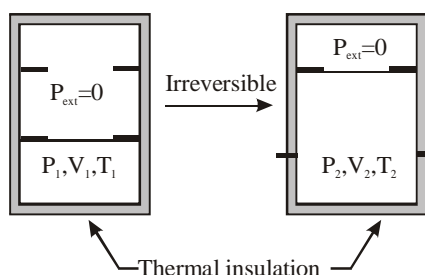
- (A) $T_1 = T_2$ (B) $T_3 > T_1$ (C) $w_{\text{isothermal}} > w_{\text{adiabatic}}$ (D) $\Delta U_{\text{isothermal}} > \Delta U_{\text{adiabatic}}$

Paragraph for Q.02 and 03

A fixed mass 'm' of a gas is subjected to transformation of states from K to L to M to N and back to K as shown in the figure. [JEE 2013]

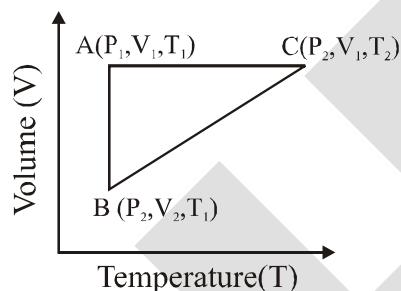


2. The pair of isochoric processes among the transformation of states is
 (A) K to L and L to M (B) L to M and N to K
 (C) L to M and M to N (D) M to N and N to K
3. The succeeding operations that enable this transformation of states are
 (A) Heating, cooling, heating, cooling (B) cooling, heating, cooling, heating
 (C) Heating, cooling, cooling, heating (D) Cooling, heating, heating, cooling
4. An ideal gas in thermally insulated vessel at internal pressure = P_1 , volume = V_1 and absolute temperature = T_1 expands irreversibly against zero external pressure, as shown in the diagram. The final internal pressure, volume and absolute temperature of the gas are P_2 , V_2 and T_2 , respectively. For this expansion, [JEE 2014]



- (A) $q = 0$ (B) $T_2 = T_1$ (C) $P_2 V_2 = P_1 V_1$ (D) $P_2 V_2^\gamma = P_1 V_1^\gamma$

5. An ideal gas is expanded from (p_1, V_1, T_1) to (p_2, V_2, T_2) under different conditions. The correct statement(s) among the following is(are) [JEE 2017]
- (A) The work done on the gas is maximum when it is compressed irreversibly from (p_2, V_2) to (p_1, V_1) against constant pressure p_1
- (B) The work done by the gas is less when it is expanded reversibly from V_1 to V_2 under adiabatic conditions as compared to that when expanded reversibly from V_1 to V_2 under isothermal conditions.
- (C) The change in internal energy of the gas (i) zero, if it is expanded reversibly with $T_1 = T_2$, and (ii) positive, if it is expanded reversibly under adiabatic conditions with $T_1 \neq T_2$
- (D) If the expansion is carried out freely, it is simultaneously both isothermal as well as adiabatic
6. A reversible cyclic process for an ideal gas is shown below. Here, P , V and T are pressure, volume and temperature, respectively. The thermodynamic parameters q , w , H and U are heat, work, enthalpy and internal energy, respectively. [JEE 2018]



The correct option(s) is (are)

- (A) $q_{AC} = \Delta U_{BC}$ and $w_{AB} = P_2 (V_2 - V_1)$ (B) $w_{BC} = P_2 (V_2 - V_1)$ and $q_{BC} = \Delta H_{AC}$
- (C) $\Delta H_{CA} < \Delta U_{CA}$ and $q_{AC} = \Delta U_{BC}$ (D) $q_{BC} = \Delta H_{AC}$ and $\Delta H_{CA} > \Delta U_{CA}$

ANSWER-KEY

EXERCISE # S-I

1. Ans. (a) $W = -P\Delta V$ (b) $W = -P\Delta V = -1(5 - 1) = -4$ litre-atm.
2. Ans. -3.1 kJ
3. Ans. (i) 9, 3, 2, 4 (ii) 9, 3, 3, 3 (iii) 3, 3, 0, 0 (iv) 12, 3, 3, 6
4. Ans. $q = -65$ J; $w = 20$ J; $\Delta U = -45$ J
5. Ans. (a) $+60$ J (b) -70 J (c), $+50$ J, $+10$ J
6. Ans. (13)
7. Ans. (140)
8. Ans. (i) 18.42 bar.L; (ii) 72 bar.L; (iii) 40 bar.L
9. Ans. (500 J)
10. Ans. $\Delta U = w = -1050$ R ; $\Delta H = -1470$ R , $q = 0$
11. Ans. 2244.78 Joule
12. Ans. $T_2 = 100$ K; $w = -5.016$ kJ
13. Ans. (7)
14. Ans. $q = 0$, $w = \Delta U = 4.125$ kJ ; $\Delta H = 5.372$ kJ ; $V_f = 11.8$ dm³ ; $P = 5.22$ atm
15. Ans. (a) $T_1 = 243.60$ K ; $T_2 = 2436$ K, (b) $\Delta U = 0$; $q = -w = 3264.24$ cal
16. Ans. (a) AC, (b) 170 J, (c) 10 J
17. Ans. $[-800$ cal]
18. Ans. (7)
19. Ans. (a) $\frac{11}{3}$ cal /K-mol. (b) 2566.67 cal (c) -466.67 cal (d) 2100 cal
20. Ans. (9)
21. Ans. -10.13 J
22. Ans. $\Delta E = 75.12$ kJ
23. Ans. $\Delta H \cong \Delta U = 1440$ calories

EXERCISE # S-II

1. Ans. (a) 600 K, (b) 3 kcal, 1.680 kcal, -1.8 kcal, -1.680 kcal (c) -1.2 kcal
2. Ans. ΔU & $\Delta H = 0$; $w = 623.55$ J ; $q = -623.55$ J
3. Ans. $w = -nRT \ln \frac{V_f}{V_i} - n^2 a \left(\frac{1}{V_f} - \frac{1}{V_i} \right)$
4. Ans. (i) $w = -8400$ cal, $q = 8400$ cal, $\Delta U = \Delta H = 0$
 (ii) $w = -2700$ cal, $q = 0$ cal, $\Delta U = -2700$, $\Delta H = -4500$ cal
 (iii) $w = 0$ cal, $q = 0$ cal, $\Delta U = 0$, $\Delta H = 0$
 (iv) $w = -1395$ cal, $q = 0$, $\Delta U = -1395$ cal, $\Delta H = -2325$ cal
 (v) $w = -2325$ cal, $q = 2325$ cal, $\Delta U = 0$, $\Delta H = 0$
5. Ans. $\Delta U = 501$ J ; $\Delta H = 99.5$ kJ
6. Ans. 100 KJ/mole
7. Ans. -1200 cal
8. Ans. 60 cal
9. Ans. (32)
10. Ans. (-900 caloricoes)
11. Ans. 7.4 atm litre
12. Ans. 35 atm
13. Ans. 3120
14. Ans. (6)

EXERCISE # O-I

- | | | | |
|-------------|-------------|-------------|-------------|
| 1. Ans.(C) | 2. Ans.(B) | 3. Ans.(C) | 4. Ans.(D) |
| 5. Ans.(C) | 6. Ans.(C) | 7. Ans.(B) | 8. Ans.(C) |
| 9. Ans.(D) | 10. Ans.(B) | 11. Ans.(D) | 12. Ans.(B) |
| 13. Ans.(C) | 14. Ans.(C) | 15. Ans.(B) | 16. Ans.(C) |
| 17. Ans.(C) | 18. Ans.(A) | 19. Ans.(A) | 20. Ans.(D) |
| 21. Ans.(A) | 22. Ans.(A) | | |

EXERCISE # O-II

- | | | | |
|---|--------------|----------------|--------------|
| 1. Ans.(A) | 2. Ans.(C) | 3. Ans.(A,B,C) | 4. Ans.(C) |
| 5. Ans.(A,B,C,D) | 6. Ans.(B,D) | 7. Ans.(B,C) | 8. Ans.(B,D) |
| 9. Ans.(C) | 10. Ans.(D) | 11. Ans.(D) | 12. Ans.(A) |
| 13. Ans.(B) | 14. Ans.(B) | 15. Ans.(A) | 16. Ans.(C) |
| 17. Ans.(A)→(P,R,S) ; (B)→(Q,S) ; (C)→(Q,S) ; (D)→(S) | | | |
| 18. Ans.(A)→(P) ; (B)→(P,Q,R) ; (C)→(P,Q,R,S,T) ; (D)→(T) | | | |
| 19. Ans.(B) | 20. Ans.(A) | | |

EXERCISE # J-MAIN

- | | | | |
|------------|------------|------------|------------|
| 1. Ans.(1) | 2. Ans.(1) | 3. Ans.(2) | 4. Ans.(1) |
| 5. Ans.(3) | 6. Ans.(2) | 7. Ans.(2) | 8. Ans.(2) |

EXERCISE # J-ADVANCED

- | | | | |
|----------------|--------------|------------|----------------|
| 1. Ans.(A,D) | 2. Ans.(B) | 3. Ans.(C) | 4. Ans.(A,B,C) |
| 5. Ans.(A,B,D) | 6. Ans.(B,C) | | |

ALLERK
Session 2019-20

THERMODYNAMICS-02

1. LIMITATION OF FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics can evaluate the value of ΔU and ΔH (i.e. energy difference between two states), but can not predict the feasibility of a process. Many processes can take place on their own and many others require an external force to carry out the process. The first law is clueless about why some processes happens on their own and why some others do not.

❖ Importance of Second law :

What is the driving force for a process which takes system from one state to other on it's own? Why such processes (*called spontaneous process*) take place at all? Answers to these questions are given by second law.

2. SPONTANEOUS PROCESS

A spontaneous process is the one which takes place on its own & can drive some other process as well. However, in some cases, initiation may be required.

Ex :

- (i) Mixing of two gases.
- (ii) Cooling of a hot object by transferring heat to surrounding.
- (iii) Water flowing down the hill.
- (iv) Rusting of iron.
- (v) Burning of coal, coke, hydrocarbons.
- (vi) Volcanic eruptions.

The synonyms of spontaneous processes are **natural processes** and irreversible processes.

It is a common observation that natural processes occur with finite rate. All spontaneous processes take place due to a finite driving force (which can be temperature difference, height difference, potential energy difference, etc.). Also the change brought about by a spontaneous process can not be restored without making some effort (which brings about permanent change in surrounding). Hence it is quite natural to call these processes as irreversible processes.

Ex :

When water flows from a dam, a part of the potential energy is converted into electrical energy and a part is converted into kinetic energy. The kinetic energy part is lost as heat energy. This loss of extra work is the permanent change in universe, because this heat energy lost cannot be completely converted back into P.E. of water.

3. Disorder :

The term 'disorder' is related to randomness. Any macroscopic property of a system is an average of large number of microscopic forces which are random in nature. Greater the randomness associated with microscopic forces, greater is the uncertainty about exact microscopic description of a macroscopic state and greater will be the disorder associated with the macroscopic state.

As a rule :

- (i) Greater the number of molecules in which a given energy is distributed, greater is the disorder.
- (ii) Greater the spread of given number of molecules with given energy in space, greater will be the disorder.

4. SECOND LAW OF THERMODYNAMICS

The entropy of the universe increases in course of every spontaneous process. The entropy of system is a state function. The change in entropy of a system is given by -

$$dS = \frac{dq_{rev}}{T} \quad \text{where ; } dq_{rev} = \text{heat exchanged by system in a very small step (reversibly).}$$

4.1 Entropy :

Entropy is a measure of disorder. The entropy is a state function and a basic quantity directly defined by second law. In every spontaneous process, entropy of universe increases.

There are three types of entropy changes :

- (i) ΔS_{System} : Entropy change of system
 - (ii) $\Delta S_{\text{Surrounding}}$: Entropy change of surrounding
 - (iii) ΔS_{Total} : Entropy change of universe
- $$\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} = \Delta S_{\text{universe}} = \Delta S_{\text{total}} = \Delta S_{\text{isolated}}$$
- Normally, ΔS means entropy change of system.

4.2 Second law in terms of entropy of universe :

For any spontaneous process (irreversible process) -

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0$$

During a reversible process -

$$\Delta S_{\text{universe}} = 0$$

Thus during irreversible process, entropy of universe increases while during reversible process, entropy of universe remains constant.

4.3 Physical significance of quantity $\frac{dq_{rev}}{T}$:

dq_{rev} = heat absorbed by the system, T = absolute temperature at which heat is absorbed. Suppose, similar quantity of heat is absorbed at two different temperatures T_1 and T_2 ($T_2 \gg T_1$). When heat is supplied at high temperature, the % age increase in kinetic energy is less compared to heat supplied at low temperature. Hence, disorder will increase by greater value, when heat is supplied at lower temperature.

4.4 Determining ' $\Delta S_{\text{surr.}}$ ' for irreversible processes :

The change in entropy is given by : $\frac{\text{heat absorbed by an entity}}{\text{Exact temperature at which heat is absorbed}}$

The irreversible processes are fast and uncontrolled. The exact temperature of system during exchange of heat cannot be known. Hence, reversible path is needed to evaluate the entropy of system. Along reversible path, the heat exchange and exact temperature both are known.

Surrounding is generally a big entity and heat absorbed by surrounding is comparatively very small as compared to its size. Hence, internal equilibrium of surrounding is not disturbed during exchange of heat.

\therefore Actual heat exchange of system is reversible heat exchange of surroundings

$\therefore (q_{\text{rev}})_{\text{surr}} = -q_{\text{irr}}$ [q_{irr} = Actual heat gained by system in a irreversible process.]

Hence, exact temperature and heat exchange both are known as far as surrounding is concerned even for an irreversible process.

\therefore **For irreverisble process :** $\Delta S_{\text{surr}} = \frac{-q_{\text{irr}}}{T}$

	ΔS_{system}	$\Delta S_{\text{surrounding}}$
(i)	For reversible process : $\Delta S_{\text{system}} = \int_{T_1}^{T_2} \frac{dq_{\text{rev}}}{T}$	For reversible process : $\Delta S_{\text{surr}} = \int_{T_1}^{T_2} \frac{dq_{\text{rev}}}{T} = -\Delta S_{\text{system}}$
(ii)	For irreversible process : $\Delta S_{\text{system}} = \int_{T_1}^{T_2} \frac{dq_{\text{rev}}}{T}$ <p>[Where ; dq_{rev} = heat gained by system for imaginary reversible path between same states]</p>	For irreversible process : $\Delta S_{\text{surr}} = -\frac{q_{\text{irr}}}{T}$
(iii)	Always evaluated along reversible path (for both reversible and irreversible process)	For reversible process, ΔS_{surr} is evaluated along reversible path, while for irreversible process, irreversible heat is used to calculate ΔS_{surr} .
(iv)	Since no actual process is reversible, ΔS_{system} is always evaluated by hypothetical path.	For hypothetical process, ΔS_{surr} is evaluated by hypothetical heat, while for real irreversible process, it is evaluated by heat exchanged in irreversible process.

5. SECOND LAW (IN TERMS OF ENGINE)

- (i) No cyclic engine is possible whose only effect is complete conversion of heat into work without making any change in surrounding on its own.
- (ii) Heat can not flow from cold body to hot body on its own without external intervention.
- (iii) Complete conversion of heat (taken from a single source) into work is not possible in a cyclic process while complete conversion of work into heat is possible in a cyclic process. Thus, heat and work are not equivalent from the view point of II law.

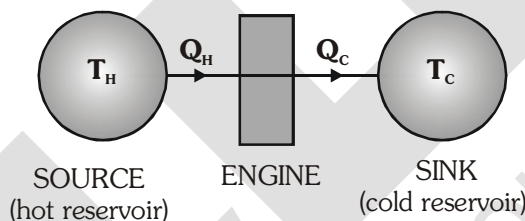
All above statements can be easily justified by realising that heat is a disordered form of energy while work is an ordered form of energy.

Complete conversion of [Heat \longrightarrow Work] on its own without any external assistance means [Disorder \longrightarrow Order] on its own - which is impossible.

5.1 Heat engine :

A heat engine is a device which can work continuously and cyclically without any external help absorbing heat from a source and rejecting a part of heat into sink. The net heat absorbed by engine (heat absorbed from source – heat given out to sink) is converted into work.

\Rightarrow Heat engine must work in cycles, otherwise it can not work continuously.



Q_H = Heat gained by engine per cycle

Q_C = Heat rejected by engine per cycle

$$\text{Efficiency of engine : } \eta = \frac{Q_H - Q_C}{Q_H} = \frac{W_{by}}{Q_H}$$

W_{by} = Work done by engine per cycle.

During operation of heat engine, heat is transferred from source (high temperature reservoir) to sink (low temperature reservoir) thus degrading the quality of energy. Note that net energy of universe remains conserved, but its quality is degraded (i.e. more disordered energy) when heat engine runs spontaneously.

5.2 CARNOT ENGINE

A carnot engine (a hypothetical engine) runs in reversible manner. Thus during expansion (work producing process) maximum work is done. However during compression (work requiring process) minimum work need to be done. Thus no engine can be more efficient than carnot engine.

The carnot engine works in following steps. (Assume ideal gas as working material).

- (i) Reversible isothermal expansion $(P_1, V_1, T_2 \rightarrow P_2, V_2, T_2)$
- (ii) Reversible adiabatic expansion $(P_2, V_2, T_2 \rightarrow P_3, V_3, T_1)$
- (iii) Reversible isothermal compression $(P_3, V_3, T_1 \rightarrow P_4, V_4, T_1)$
- (iv) Reversible adiabatic compression $(P_3, V_3, T_1 \rightarrow P_1, V_4, T_2)$

Now: $Q_{NET} = -w_{NET}$

$$w_{NET} = w_{12} + w_{23} + w_{34} + w_{41}$$

$$w_{12} = -nRT_H \ln \left(\frac{V_2}{V_1} \right)$$

$$w_{23} = nC_V (T_C - T_H)$$

$$w_{34} = -nRT_C \ln \left(\frac{V_4}{V_3} \right)$$

$$w_{41} = -nC_V (T_H - T_C)$$

Also since process 2 – 3 and 4 – 1 are reversible adiabatic process.

$$T_H V_2^{\gamma-1} = T_C V_3^{\gamma-1}$$

$$T_C V_1^{\gamma-1} = T_H V_4^{\gamma-1}$$

from above equations

$$\left(\frac{V_2}{V_1} \right) = \left(\frac{V_3}{V_4} \right)$$

Substituting the value of $\left(\frac{V_4}{V_3} \right)$ in eq.(v) and adding w in individual step.

$$w_{NET} = -nRT_H \ln \left(\frac{V_2}{V_1} \right) + nC_V (T_C - T_H) - nRT_C \ln \left(\frac{V_4}{V_3} \right) - nC_V (T_C - T_H)$$

$$w_{NET} = -nRT_H \ln \left(\frac{V_2}{V_1} \right) - nRT_C \ln \left(\frac{V_1}{V_2} \right)$$

$$w_{NET} = -nR [T_C - T_H] \ln \left(\frac{V_2}{V_1} \right)$$

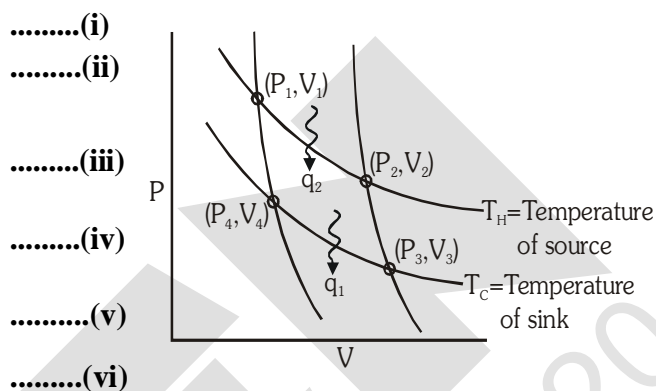
$$\Rightarrow \text{Efficiency } \eta = -\frac{w_{NET}}{q_2}$$

$$\eta = \frac{nR \ln \left(\frac{V_2}{V_1} \right) [T_H - T_C]}{nRT_H \ln \left(\frac{V_2}{V_1} \right)}$$

$$\therefore \eta = \frac{T_H - T_C}{T_H}$$

Thus efficiency of carnot engine depends only upon temperature of source and sink.

Note : If working substance is changed (eg. ideal gas by real gas) efficiency of carnot engine remains unaffected.



.....(vii) for process 2 – 3

.....(viii) for process 1 – 4

.....(ix)

EXERCISE # 1

1. A heat engine absorbs 760 kJ heat from a source at 380K. It rejects (i) 650 kJ, (ii) 560 kJ, (iii) 504 kJ of heat to sink at 280K. State which of these represent a reversible, an irreversible or an impossible cycle.
2. The maximum efficiency of a heat engine operating between 100°C and 25°C is :-
(A) 20.11% (B) 22.2% (C) 25.17% (D) None
3. A carnot engine operating between 227°C and 27°C absorbs 2 Kcal of heat from the 227°C reservoir reversibly per cycle. The amount of work done in one cycle is :-
(A) 0.4 Kcal (B) 0.8 Kcal (C) 4 Kcal (D) 8 Kcal
4. An ideal gas heat engine operates in carnot's cycle between 227°C and 127°C. It absorbs 6×10^4 cal of heat at high temperature. Amount of heat converted to work is :
(A) 2.4×10^4 cal (B) 4.8×10^4 cal (C) 1.2×10^4 cal (D) 6.0×10^4 cal

6. ENTROPY CHANGE OF AN IDEAL GAS

From definition of entropy of system -

$$dS_{\text{system}} = \frac{dq_{\text{rev}}}{T} \quad \text{.....(i)}$$

from first law, $dq_{\text{rev}} = dU + PdV$

For a reversible change involving an ideal gas -

$$dq_{\text{rev}} = nC_{V,m}dT + \frac{nRT}{V}dV \quad \text{.....(ii)}$$

$$\Rightarrow \int_1^2 \frac{dq_{\text{rev}}}{T} = \int_1^2 \frac{nC_{V,m}dT}{T} + \int_{V_1}^{V_2} nR \frac{dV}{V}$$

$$\Delta S_{\text{system}} = nC_{V,m} \ln \frac{T_2}{T_1} + nR \ln \left(\frac{V_2}{V_1} \right) = nC_{p,m} \ln \frac{T_2}{T_1} - nR \ln \frac{P_2}{P_1}$$

Note : This formula is applicable to all ideal gas process.

6.1 Ideal gas processes :

(i) For isothermal change :

$$\Delta S = \int_1^2 \frac{dq_{\text{rev}}}{T} = \frac{1}{T} \int_1^2 dq_{\text{rev}} \quad (\because T = \text{constant})$$

$$\Rightarrow \Delta S = \frac{q_{\text{rev}}}{T} = nR \ln \frac{V_2}{V_1} \quad \left[\because q_{\text{rev}} = nRT \ln \left(\frac{V_2}{V_1} \right) \right]$$

(ii) For isochoric change :

$$\Delta S = \int_1^2 \frac{dq_v}{T} = \int_1^2 \frac{nC_{V,m}dT}{T} = nC_{V,m} \int_1^2 \frac{dT}{T} \quad [\because dq_v = nC_{V,m}dT]$$

$$\Rightarrow \Delta S = nC_{V,m} \ln \frac{T_2}{T_1}$$

(iii) For isobaric change :

$$\Delta S = \int_1^2 \frac{dq_p}{T} = \int_1^2 \frac{nC_{p,m}dT}{T} = nC_{p,m} \int_1^2 \frac{dT}{T} \quad [\because dq_p = nC_{p,m}dT]$$

$$\Rightarrow \Delta S = nC_{p,m} \ln \left(\frac{T_2}{T_1} \right)$$

(iv) **Reversible adiabatic process :**

$$q_{\text{rev}} = 0$$

$$\Rightarrow \Delta S = \underbrace{nC_v \ln \frac{T_2}{T_1}}_{\text{entropy change due to change in temperature}} + \underbrace{nR \ln \frac{V_2}{V_1}}_{\text{entropy change due to change in volume}} = 0$$

(a) **During reversible adiabatic expansion :**

$$T_2 < T_1 \text{ and } V_2 > V_1$$

\Rightarrow Sign of two terms are opposite and magnitudes are same because for reversible adiabatic process -

$$nC_{v,m} \ln \frac{T_2}{T_1} = -nR \ln \frac{V_2}{V_1}$$

\Rightarrow +ive and -ive term cancel out each other and hence, $\Delta S = 0$

Thus, decrease in entropy during expansion due to decrease in temperature is exactly cancelled out by increase in entropy due to increase in volume of system in reversible adiabatic expansion.

(b) **During reversible adiabatic compression :**

$$T_2 > T_1 \text{ and } V_2 < V_1$$

$$\Rightarrow \Delta S_{\text{Total}} = \underbrace{nC_{v,m} \ln \frac{T_2}{T_1}}_{\text{+ive}} + \underbrace{nR \ln \frac{V_2}{V_1}}_{\text{? ive}} = 0$$

Thus, increase in entropy due to increase in temperature is compensated by decrease in entropy due to decrease in volume of system in reversible adiabatic compression.

Hence, $\Delta S = 0$ for reversible adiabatic compression.

(v) **Irreversible adiabatic process :**

Since process is irreversible, $\Delta S_{\text{Total}} > 0$.

$$\Rightarrow \Delta S_{\text{system}} + \Delta S_{\text{surr}} > 0$$

$$\therefore \Delta S_{\text{surr}} = 0$$

$$\therefore \Delta S_{\text{system}} > 0$$

The physical interpretation is -

(a) During irreversible adiabatic compression, large quantity of heat is produced while decrease in volume is less.

Thus, increase in entropy due to rise in temperature exceeds the decrease in entropy due to decrease in volume. Hence net entropy change is positive.

(b) During irreversible adiabatic expansion, due to sudden decrease in external pressure, the system remains less challenged during expansion. Hence system do less work-resulting in lesser decrease in temperature.

The increase in volume of system is relatively larger (because system was less challenged)

Thus increase in entropy due to increase in volume exceeds decrease in entropy due to decrease in temperature. The net change in entropy is positive in both processes $\Delta S_{\text{surr.}} = 0$ (\because no heat is exchanged with surrounding) and $\Delta S_{\text{total}} > 0$.

(vi) Free expansion of an ideal gas against vacuum :

Free expansion of an ideal gas is an example of irreversible adiabatic as well as irreversible isothermal process.

During free expansion, the $P_{\text{ext.}} = 0$. Hence, the ideal gas is not challenged at all during expansion. The kinetic energy of ideal gas remains constant. Hence, no temperature difference is created during expansion between system and surrounding.

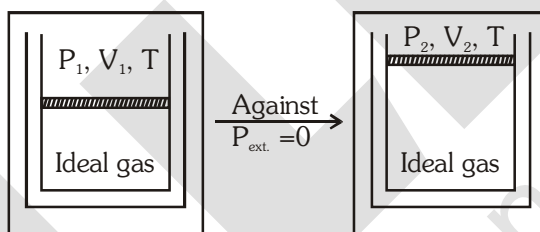
$\because \Delta T = 0$, the heat absorbed during the process = 0

Since, $V_f > V_i$ and $T = \text{constant}$, $\Delta S_{\text{system}} > 0$

The free expansion is an example where $q_{\text{actual}} = 0$, still $\Delta S_{\text{system}} > 0$.

This is reasonable, because : $\Delta S_{\text{system}} = \int \frac{dq_{\text{rev.}}}{T}$

This, example clearly shows that even if q_{actual} between two states is zero, this does not mean that $\int_1^2 \frac{dq_{\text{rev.}}}{T}$ between two states is zero. This outlines the importance of reversible path and $q_{\text{rev.}}$ in calculation of entropy of system.



$$q_{\text{irr}} = 0 ; w_{\text{irr}} = 0$$

$$\Delta S_{\text{system}} = \int_1^2 \frac{dq_{\text{rev.}}}{T} = nR \ln \frac{V_2}{V_1}$$

$$\Delta S_{\text{surr.}} = \frac{-q_{\text{irr}}}{T} = 0$$

$$\Delta S_{\text{total.}} = nR \ln \frac{V_2}{V_1} > 0$$

ENTROPY CALCULATION

Process	$\Delta S_{\text{Sys.}}$	$\Delta S_{\text{Surr.}}$
Isothermal reversible	$\Delta S_{\text{Sys.}} = nR \ln \frac{V_2}{V_1}$	$\Delta S_{\text{Surr.}} = -\Delta S_{\text{Sys.}}$
Isothermal irreversible	$\Delta S_{\text{Sys.}} = nR \ln \frac{V_2}{V_1}$	$\Delta S_{\text{Surr.}} = \frac{-q_{\text{sys}}}{T} = \frac{W_{\text{Sys}}}{T} = \frac{-P_{\text{ext}}(V_2 - V_1)}{T}$
Adiabatic reversible	$\Delta S_{\text{Sys.}} = 0$	$\Delta S_{\text{Surr.}} = 0$
Adiabatic irreversible	$\Delta S_{\text{Sys.}} = nC_{P,m} \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$	$\Delta S_{\text{Surr.}} = 0$
Isochoric reversible	$\Delta S_{\text{Sys.}} = nC_{V,m} \ln \frac{T_2}{T_1}$	$\Delta S_{\text{Surr.}} = -\Delta S_{\text{Sys.}}$
Isochoric irreversible	$\Delta S_{\text{Sys.}} = nC_{V,m} \ln \frac{T_2}{T_1}$	$\Delta S_{\text{Surr.}} = \frac{-q_{\text{sys}}}{T_{\text{surr}}} = \frac{-nC_{V,m} \Delta T}{T_{\text{final}}}$

Ex.1 Three moles of an ideal gas is expanded isothermally from 2L to 10L, at 27°C. Calculate ΔS_{sys} and ΔS_{surr} and $\Delta S_{\text{univ.}}$ if the process is preformed.

(i) Reversibly

(ii) Irreversibly, against a constant external pressure of 1 atm

(iii) As free expansion

Sol: (i) $\Delta S_{\text{univ.}} = 0$, $\Delta S_{\text{surr.}} = -\Delta S_{\text{sys.}}$

$$\text{and } \Delta S_{\text{sys}} = nR \ln \frac{V_2}{V_1} = 3R \cdot \ln \frac{10}{2} = 40.14 \text{ J/K}$$

(ii) $\Delta S_{\text{sys}} = 40.14 \text{ J/K}$

$$\Delta S_{\text{surr.}} = -\frac{P_{\text{ext.}}(V_2 - V_1)}{T} = -\frac{1 \times (10 - 2) \times 101.3}{300} = -2.7 \text{ J/K}$$

$$\text{and } \Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 37.44 \text{ J/K}$$

(iii) $\Delta S_{\text{sys}} = 40.14 \text{ J/K}$

$$\Delta S_{\text{surr.}} = 0 \quad \text{as } P_{\text{ext}} = 0$$

$$\text{and } \Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 40.14 \text{ J/K}$$

Ex.2. Two moles of an ideal monoatomic gas is expanded adiabatically from 10L, 27°C to 80L. Calculate ΔS_{sys} , ΔS_{surr} and ΔS_{univ} , if the process is performed.

(i) Reversibly

(ii) Irreversibly, against a constant external pressure of 0.1 atm.

(iii) As free expansion

Sol.: $\Delta S_{surr} = 0$ for all

(i) $\Delta S_{sys} = \Delta S_{surr} = \Delta S_{univ} = 0$

(ii) $n \cdot C_{v,m} \cdot (T_2 - T_1) = -P_{ext}(V_2 - V_1)$

or $2 \times \frac{3}{2} \times 0.0821 \times (T_2 - 300) = -0.1 \times (80 - 10) \Rightarrow T_2 = 271.58 \text{ K}$

Now, $\Delta S_{sys} = n \cdot C_{v,m} \cdot \ln \frac{T_2}{T_1} + nR \cdot \ln \frac{V_2}{V_1}$
 $= 2 \times \frac{3}{2} R \times \ln \frac{271.58}{300} + 2 \times R \times \ln \frac{80}{10} = 32.90 \text{ J/K}$

and $\Delta S_{univ} = \Delta S_{sys}$

(iii) $T_1 = T_2 \Rightarrow \Delta S_{sys} = nR \cdot \ln \frac{V_2}{V_1} = 2 \times R \times \ln \frac{80}{10} = 34.58 \text{ J/K}$

6.2 Entropy change of solids and liquids upon heating :

$$\Delta S = \int \frac{dq_{rev}}{T} = \int \frac{mS \cdot dT}{T} = mS \cdot \ln \frac{T_2}{T_1} \quad [S = \text{specific heat of solid/ liquid}]$$

For molar change in entropy, $m = M(\text{g/mole})$; where M = molar mass.

Note, for solids and liquids ($MS \cong C_p \cong C_v$)

Ex.3 Two blocks of equal masses and heat capacity but at different temperatures are taken in an adiabatic vessel. Show that total change in entropy when both attain thermal equilibrium is always positive.

Sol. Let the temperature of hot body be T_H , temperature of cold body be T_C & the final temperature be T_F .

Now, net heat exchanged by two bodies must be zero.

$$\Rightarrow m \cdot S (T_F - T_H) + mS (T_F - T_C) = 0$$

$$\Rightarrow T_F = \frac{T_H + T_C}{2}$$

Since both bodies are of finite mass, entropy of both bodies are evaluated by reversible paths.

$$\Delta S_{Hot} = \int_{T_H}^{T_F} mS \cdot \frac{dT}{T} = mS \cdot \ln \frac{T_F}{T_H}$$

$$\Delta S_{Cold} = \int_{T_C}^{T_F} mS \cdot \frac{dT}{T} = mS \cdot \ln \frac{T_F}{T_C}$$

$$\Rightarrow \Delta S_{\text{total}} = (mS) \ln \left(\frac{T_F^2}{T_H T_C} \right)$$

$$\Rightarrow T_H^2 + T_C^2 + 2T_H T_C - 4T_H T_C = (T_H - T_C)^2 > 0$$

$$\Rightarrow (T_H + T_C)^2 > 4T_H T_C$$

$$\Rightarrow \Delta S_{\text{total}} > 0$$

6.3 Reversible phase transitions :

Reversible phase transitions are always isothermal & isobaric.

$$\Delta S_{\text{system, P,T}} = \frac{q_{\text{rev.}}}{T} = \frac{\Delta H_{\text{P,T}}}{T_{\text{Transition}}}$$

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{P,T}}}{T_{\text{Transition}}}$$

$$\Delta S_{\text{total}} = 0$$

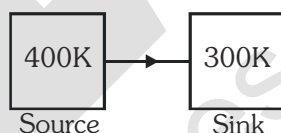
Thus, $\Delta S_{\text{vaporisation}}$ at boiling point = $\frac{\Delta H_{\text{vaporisation}}}{T_{\text{vaporisation}}}$

$$\Delta S_{\text{fusion}}$$
 at melting point = $\frac{\Delta H_{\text{fusion}}}{T_{\text{fusion}}}$

$$\Delta S_{\text{sublimation}}$$
 at sublimation point = $\frac{\Delta H_{\text{sublimation}}}{T_{\text{sublimation}}}$

$$\Delta S_{\text{allotropic modification}} = \frac{\Delta H_{\text{allotropic modification}}}{T_{\text{transition}}}$$

Ex.4 100 kJ heat is transferred from a larger heat reservoir at 400 K to another large heat reservoir at 300 K. Suppose there is no change in temperature due to exchange of heat :



Find ΔS_{source} , ΔS_{sink} and ΔS_{total} . Comment on spontaneity of process.

Ans. (i) $\Delta S_{\text{source}} = \frac{\text{heat absorbed by source}}{\text{Temperature of source}}$

$$\Delta S_{\text{source}} = \frac{-100\text{kJ}}{400} = -250\text{J/K}$$

(ii) $\Delta S_{\text{sink}} = \frac{\text{heat absorbed by sink}}{\text{Temperature of sink}}$

$$= \frac{+100000\text{J}}{300} = 333.33\text{J/K}$$

(iii) $\Delta S_{\text{Total}} = \Delta S_{\text{source}} + \Delta S_{\text{sink}} = +83.33\text{J/K}$

Ex.5 Trouton's rule states that the ratio of the molar heat of vaporisation of a liquid to its normal

boiling point is approximately the same for all liquids, $\frac{\Delta H_{\text{vap}}}{T_{\text{bp}}} = 88 \text{ JK}^{-1} \text{ mol}^{-1} = \Delta S_{\text{vap}}$.

Which of the following liquids do not follow Trouton's rule : NH_3 , C_6H_6 , CCl_4 , CHCl_3 , Hg . Explain.

Ans. NH_3 , due to H-bonding : $\Delta S_{\text{vap}} > 88 \text{ J/K-mol}$

EXERCISE # 2

5. Identify the correct statement regarding a spontaneous process :- [AIEEE-2007]
 (A) For a spontaneous process in an isolated system, the change in entropy is positive
 (B) Endothermic processes are never spontaneous
 (C) Exothermic processes are always spontaneous
 (D) Lowering of energy in the reaction process is the only criterion for spontaneity
6. Find the change in entropy (in cal/k) of 1 mole of O_2 gas ($C_V = 5/2 R$), when it is
 (a) heated from 300 K to 400 K isobarically
 (b) heated from 300 K to 400 K isochorically (Given : $\ln 3 = 1.1$, $\ln 2 = 0.7$)
7. One mole of NaCl(s) on melting at its melting point absorbed 32.76 kJ of heat and its entropy is increased by 30 JK^{-1} . What is the melting point of sodium chloride ?
8. The entropy change when two moles of ideal monoatomic gas is heated from 200°C to 300°C reversibly and isochorically :-
 (A) $\frac{3}{2}R \ln\left(\frac{300}{200}\right)$ (B) $\frac{5}{2}R \ln\left(\frac{573}{273}\right)$ (C) $3R \ln\left(\frac{573}{473}\right)$ (D) $\frac{3}{2}R \ln\left(\frac{573}{473}\right)$
9. Predict the sign entropy change for the following processes:
 (A) $\text{O}_2(\text{g}) \rightarrow 2\text{O}(\text{g})$ (B) $2\text{O}_3(\text{g}) \rightarrow 3\text{O}_2(\text{g})$
 (C) $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$ (D) $\text{NaCl(s)} \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$
 (E) $\text{C}_2\text{H}_5\text{OH(l)} \rightarrow \text{C}_2\text{H}_5\text{OH(g)}$ (F) $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl(s)}$
10. 5 mole of an ideal gas expands reversibly from a volume of 8 dm^3 to 80 dm^3 at a constant temperature of 27°C . The change in entropy is :-
 (A) 41.57 JK^{-1} (B) -95.73 JK^{-1} (C) 95.73 JK^{-1} (D) -41.57 JK^{-1}
11. ΔS for the reaction ; $\text{MgCO}_3(\text{s}) \longrightarrow \text{MgO(s)} + \text{CO}_2(\text{g})$ will be :
 (A) 0 (B) -ve (C) +ve (D) ∞
12. Change in entropy is negative for :-
 (A) Bromine (ℓ) \longrightarrow Bromine (g)
 (B) $\text{C(s)} + \text{H}_2\text{O(g)} \longrightarrow \text{CO(g)} + \text{H}_2(\text{g})$
 (C) $\text{N}_2(\text{g}, 10 \text{ atm}, 298 \text{ K}) \longrightarrow \text{N}_2(\text{g}, 1 \text{ atm}, 298 \text{ K})$
 (D) $\text{Fe(at } 400 \text{ K)} \longrightarrow \text{Fe(at } 300 \text{ K)}$
13. For which reaction from the following, ΔS will be maximum ?
 (A) $\text{Ca(s)} + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{CaO(s)}$ (B) $\text{CaCO}_3(\text{s}) \longrightarrow \text{CaO(s)} + \text{CO}_2(\text{g})$
 (C) $\text{C(s)} + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$ (D) $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{NO(g)}$
14. When two gases are mixed the entropy :-
 (A) Remains constant (B) Decreases (C) Increases (D) Becomes zero

15. For the process, $\text{CO}_2(\text{s}) \longrightarrow \text{CO}_2(\text{g})$:

- (A) Both ΔH and ΔS are +ve
(B) ΔH is -ve and ΔS is +ve
(C) ΔH is +ve and ΔS is -ve
(D) Both ΔH and ΔS are -ve

7. THIRD LAW OF THERMODYNAMICS

“At absolute zero, the entropy of a perfectly crystalline substance is zero”, which means that at absolute zero, every crystalline solid is in a state of perfect order and its entropy should be zero. By virtue of the third law, the absolute value of entropy (unlike absolute value of enthalpy) for any pure substance can be calculated at room temperature.

$$S_T - S_{0K} = \int_0^T \frac{q_{\text{rev}}}{T}$$

Since $S_{0K} = 0$

$$S_T = \int_0^T \frac{q_{\text{rev}}}{T}$$

The variation of entropy of a substance with temperature is given by graph :

At 1, entropy of substance is zero.

- **from 1-2** ; The temperature of solid increases upon heating -

$$\Rightarrow S_2 - S_1 = \int \frac{C_{P, \text{solid}}}{T} dT \quad \text{.....(i)}$$

- **from 2-3** ; The temperature remains constant during phase transition.

$$\Rightarrow S_3 - S_2 = \Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T_f} \quad \dots\dots(\text{ii})$$

- **from 3-4 ;** The temperature of liquid increases

$$\Rightarrow S_4 - S_3 = \int_{T_3}^{T_4} \frac{C_{p, \text{liquid}} \cdot dT}{T} \quad \text{.....(iii)}$$

- **from 4-5 ;** Reversible vaporisation takes place at constant temperature -

$$\Rightarrow S_5 - S_4 = \Delta S_{\text{vap.}} = \frac{\Delta H_{\text{vap.}}}{T_b} \quad \dots\dots(\text{iv})$$

- **from 5-6 ;** The gas is heated -

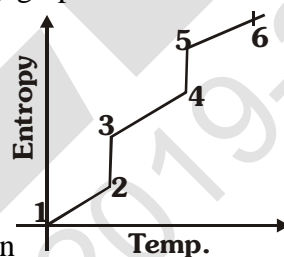
$$\Rightarrow S_6 - S_5 = \int_{T_c}^{T_6} \frac{C_{p, \text{gas}} dT}{T} \quad \dots\dots(\mathbf{v})$$

$$\Delta S_{1-6} = (S_2 - S_1) + (S_3 - S_2) + (S_4 - S_3) + (S_5 - S_4) + (S_6 - S_5) = S_6 - S_1 \quad [\because S_1 = 0]$$

$\therefore S_6 = \text{absolute entropy at 6.}$

$$= \int_{T_1}^{T_2} \frac{C_{P,\text{Solid}} dT}{T} + \frac{\Delta H_{\text{fusion}}}{T_f} + \int_{T_3}^{T_4} \frac{C_{P,\text{liquid}} dT}{T} + \frac{\Delta H_{\text{vap}}}{T_b} + \int_{T_5}^{T_6} \frac{C_{P,\text{gas}} dT}{T}$$

- **Comment :** Absolute entropy of a substance can be calculated using third law by reversible path.



Change in entropy of a pure substance with temperature at constant pressure.

7.1 Standard absolute molar entropy :

It is the entropy in one mole of substance at standard temperature at 1 bar.

It is calculated assuming that substance is heated isobarically and reversibly at 1 bar from 0 K to standard temperature.

7.2 Comparing absolute entropies of substance :

(i) The absolute entropies of substance follow the order,

$$S(g) \gg S(l) > S(s)$$

(ii) Entropy increases when solid and liquid is dissolved into solvent,

e.g.	CH ₃ OH(l)	S° = 127 J/K-mole
	CH ₃ OH(aq)	S° = 132.3 J/K-mole
	NaCl(s)	S° = 72.4 J/K-mole
	NaCl(aq.)	S° = 115.4 J/K-mole

(iii) The entropy of dissolved gas is less than pure gas.

e.g.	HCl(g)	S° = 186.7 J/K-mole
	HCl(aq)	S° = 55.2 J/K-mole

(iv) Entropy rises with increasing mass, (if other factors are similar).

e.g.	F ₂ (g)	S° = 203 J/K-mole
	Cl ₂ (g)	S° = 223 J/K-mole
	Br ₂ (g)	S° = 245 J/K-mole

(v) Entropy is lower in covalently bonded solids, with strong directional bonds, than in solids with partial metallic character.

e.g.	C(diamond)	S° = 2.44 J/K-mole
	C(graphite)	S° = 5.69 J/K-mole
	Sn(gray)	S° = 44.8 J/K-mole
	Sn(white)	S° = 51.5 J/K-mole

(vi) Entropy increases with increasing softness and with weakness of bonds between atoms.

e.g.	C(diamond)	Be(s)	S ₁ O ₂ (s)	Pb(s)	Hg(l)
	2.44	9.54	41.8	64.9	77.4
	diamond	hard metal	quartz	soft metal	liquid

(vii) Entropy increases with chemical complexity

Sub.	NaCl	MgCl ₂	AlCl ₃
	72.4	89.5	167

For CuSO₄.nH₂O

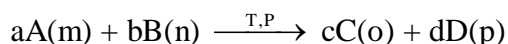
n = 0	n = 1	n = 3	n = 5
S° = 113	150	225	305

Note : Above data is given in SI unit.

7.3 Entropy change ($\Delta_r S$) of a chemical reaction :

The change in entropy when reactants turn into products according to a balanced chemical reaction with specified physical state of each reactant and product is called entropy of reaction.

• **Consider a reaction :**



where m, n, o, p are physical states at temperature T and pressure P.

$$\Delta_r S = \sum S(\text{products}) - \sum S(\text{reactants})$$

$$\Delta_r S = cS_C + dS_D - aS_A - bS_B$$

S_A, S_B, S_C and S_D are absolute molar entropies at temperature T and pressure P (from third law)

So, $\Delta_r S$ is evaluated from table of data of third law entropies of various substances.

7.4 $\Delta S_{\text{Surrounding}}$ for chemical reaction :

$\Delta_r H = q_p$ = heat absorbed by the system during chemical reaction.

$\Rightarrow -\Delta_r H = -q_p = q_{\text{surr}}$ = heat absorbed by the surrounding.

Now,

$$\Delta S_{\text{Surr}} = \frac{q_{\text{surr}}}{T} = -\frac{\Delta_r H}{T}$$

If $\Delta_r H = \text{-ive}$ (exothermic) heat is lost by the system and gained by the surrounding. Hence, ΔS_{surr} increases.

If $\Delta_r H = \text{+ive}$ (endothermic process), entropy of surrounding decreases.

$$\therefore \Delta S_{\text{surr}} = -\frac{\Delta_r H}{T} = \text{-ive}$$

- We can not comment on entropy change of system from knowledge of $\Delta_r H$. The entropy change of system ($\Delta_r S$) is estimated by third law.

7.5 Driving force of a spontaneous chemical process :

The driving force of a spontaneous chemical process is increase in entropy of universe.

In simple terms, negative value of $\Delta_r H$ and positive value of $\Delta_r S$ favours the chemical process.

If $\Delta_r H$ is positive, the enthalpy factor don't support the forward process. Under these conditions, $\Delta_r S$ should be sufficiently positive to drive the reaction in forward direction. If $\Delta_r H$ is +ive and $\Delta_r S$ is -ive, under a given situation, the process become non-spontaneous because both factors tends to decrease the entropy of the universe.

7.6 Prediction the sign of $\Delta_r S$ by inspecting a balanced chemical reaction.

(i) If more no. of gaseous moles are present on product side, $\Delta_r S$ will be +ive (since gas is more disordered than solid or liquid).

(ii) If

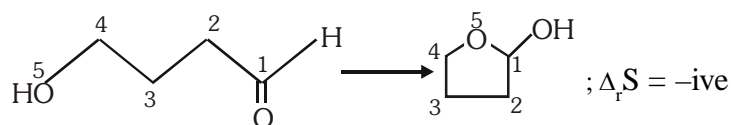
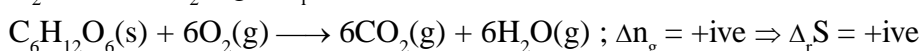
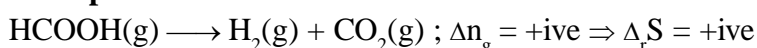
solid	\longrightarrow	liquid
solid	\longrightarrow	gas
liquid	\longrightarrow	gas

then, $\Delta_r S = \text{+ive}$.

(iii) If a molecule is undergoing cyclisation, it's rotational modes of motion are replaced by vibrational modes of motion.

Since quantum energy separation of rotational motion is closely spaced compared to vibrational energy state, rotational energy is more disordered. Hence, $\Delta_r S = \text{-ive}$.

Example :



7.7 Table for spontaneity of chemical process and sign of $\Delta_r H$, $\Delta_r S$ and dependence on temperature.

Sign of ΔH	Sign of ΔS	Comment	Example	ΔH_{298}°	ΔS_{298}°
–	+	Spontaneous at all temperature	$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$ $C(s) + O_2(g) \rightarrow CO_2(g)$	–185 –394	14.1 3
–	–	Spontaneous at low temperature	$H_2(g) + 1/2 O_2(g) \rightarrow H_2O(l)$ $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$	–44 –198	–119 –187
+	+	Spontaneous at high temperature	$NH_4Cl(s) \rightarrow NH_3(g) + HCl(g)$ $N_2(g) + O_2(g) \rightarrow 2NO(g)$	176 180	284 25
+	–	Non spontaneous at all temperature	$3O_2 \rightarrow 2O_3$ $2H_2O(l) + O_2(g) \rightarrow 2H_2O_2(l)$	286 196	–137 –126

7.8 State of equilibrium :

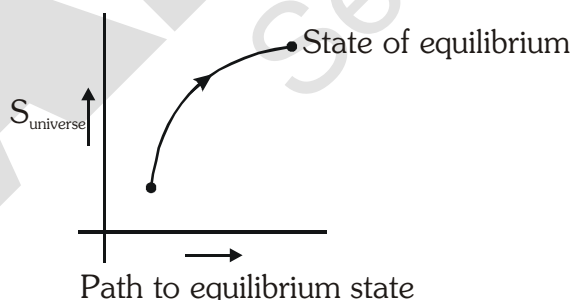
A system at equilibrium is a stable system. Hence, its state variables become constant (do not vary with time) at equilibrium.

If a system is in non-equilibrium state, it moves spontaneously in the direction of equilibrium (because the equilibrium state is stable). During the spontaneous movement towards equilibrium, the entropy of universe increases.

As the system gets closer to equilibrium state, the driving force to attain equilibrium becomes small and so does the increase in disorder of universe. At equilibrium, the driving force to move ahead finishes and entropy of the universe can not increase further.

In nutshell, when a system attains equilibrium, its capacity to increase the disorder of universe is lost.

- At equilibrium, the entropy of universe is maximum.



8. GIBB'S FUNCTION

Gibb's function 'G' is defined as $G = H - TS$.

Since 'G' is a combination of state variables (a compound state variable), it is a state function. The dimension of Gibb's function is the dimension of energy. 'G' is an extensive quantity.

Gibb's function provide a very useful criteria for spontaneity of a process taking place at constant temperature and pressure (isobaric, isothermal process).

The entropy of universe is also a very useful criteria of spontaneity, but it is based on properties of system as well as surrounding.

The Gibb's function provides criteria for spontaneity based only on the properties of system.

$$\Delta G = \Delta H - \Delta(TS)$$

$$\Delta G = \Delta H - T\Delta S$$

(Isothermal process)

Ex.6 The thermodynamic stability of a substance is dependent upon the value of Gibb's function. Explain the stability of solid at low temperature and stability of gas at very high temperature.

Sol. Any stable state tries to minimise its enthalpy while maximising its entropy.

For solids - $G_{\text{solid}} = H_{\text{solid}} - TS_{\text{solid}}$ (at certain T & P)

For liquids - $G_{\text{liquid}} = H_{\text{liquid}} - TS_{\text{liquid}}$ (at certain T & P)

For gas - $G_{\text{gas}} = H_{\text{gas}} - TS_{\text{gas}}$ (at certain T & P)

At any given T and P, $H_{\text{solid}} < H_{\text{liquid}} < H_{\text{gas}}$

and $S_{\text{solid}} < S_{\text{liquid}} < S_{\text{gas}}$

At very low temperature, TS term contributes very little towards Gibb's function. Hence -

$$G_{\text{solid}} < G_{\text{liquid}} < G_{\text{gas}} \quad (\text{at very low temperature}).$$

This explains why solids are most stable at low temperature.

At very high temperature, TS term is very important. Since S_{gas} is large, for gas TS term becomes very large at large temperature. Hence -

$\Rightarrow G_{\text{solid}} > G_{\text{liquid}} > G_{\text{gas}}$ (at very high temperature). Thus, gaseous state is most stable at high temperature.

Hence, the low enthalpies of solid are responsible for stability of solid at low temperature, while high entropy of gas is responsible for stability of gas at high temperature.

8.1 $\Delta G_{T,P}$ and $\Delta S_{\text{universe}}$

Decrease in Gibb's function at constant temperature and pressure is related to ΔS_{total} (total entropy change of system and surrounding).

$$-\Delta G = T(\Delta S_{\text{total}})$$

At constant P, T

if $\Delta G < 0 \Rightarrow$ spontaneous process

if $\Delta G > 0 \Rightarrow$ non-spontaneous process

if $\Delta G = 0 \Rightarrow$ reversible process

At constant P, T, Gibbs energy of a system spontaneously decreases.

EXERCISE # 3

16. Animals operate under conditions of constant pressure and most of the processes that maintain life are electrical (in a broad sense). How much energy is available for sustaining this type of muscular and nervous activity from the combustion of 1 mol of glucose molecules under standard conditions at 37°C (blood temperature) ? The entropy change is + 210 JK⁻¹ for the reaction as stated.

$$\Delta H_{\text{combustion [glucose]}} = -2808 \text{ kJ / mol.}$$

17. Which of the following pairs of a chemical reaction is certain to result in a spontaneous reaction?
 (A) endothermic and decreasing disorder (B) exothermic and increasing disorder
 (C) endothermic and increasing disorder (D) exothermic and decreasing disorder
18. Standard entropy of X₂, Y₂ and XY₃ are 60, 40 and 50 JK⁻¹mol⁻¹, respectively. for the reaction,
 $\frac{1}{2}X_2 + \frac{3}{2}Y_2 \rightarrow XY_3$, $\Delta H = -30 \text{ kJ}$ to be at equilibrium, the temperature will be :-
 (A) 1250 K (B) 500 K (C) 750 K (D) 1000 K
19. For a particular reversible reaction at temperature T, ΔH and ΔS were found to be both +ve. If T_e is the temperature at equilibrium, then reaction would be spontaneous when :-
[AIEEE-2010]
 (A) T = T_e (B) T_e > T (C) T > T_e (D) T_e is 5 times T
20. For a reaction at 25°C, enthalpy change (ΔH) and entropy change (ΔS) are $-11.7 \times 10^3 \text{ J mol}^{-1}$ and $-105 \text{ J mol}^{-1} \text{ K}^{-1}$ respectively. The reaction is :
 (A) Spontaneous (B) Non spontaneous (C) At equilibrium (D) Can't say anything
21. Identify the correct statement for change of Gibbs energy for a system at constant temperature and pressure.
 (A) If $\Delta G_{\text{system}} > 0$, the process is spontaneous.
 (B) If $\Delta G_{\text{system}} = 0$, the system has attained equilibrium.
 (C) If $\Delta G_{\text{system}} = 0$, the system is still moving in a particular direction.
 (D) If $\Delta G_{\text{system}} < 0$, the process is non spontaneous.
22. In conversion of lime-stone to lime, $\text{CaCO}_3(\text{s}) \longrightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
 the values of ΔH° and ΔS° are +179.1 kJ mol⁻¹ and 160.2 J/K respectively at 298 K and 1 bar. Assuming that ΔH° and ΔS° do not change with temperature, temperature above which conversion of limestone to lime will be spontaneous is :-
[AIEEE-2007]
 (A) 1008 K (B) 1200 K (C) 845 K (D) 1118 K

8.2 CALCULATE ΔG FOR VARIOUS PROCESSES

- (i) **Ideal gas subjected to isothermal compression or expansion :**

For isothermal process :

$$\Delta G = \Delta H - T\Delta S$$

For ideal gas, $\Delta H = nC_{p,m}\Delta T = 0$

(As $\Delta T = 0$, for isothermal change)

$$\& \quad \Delta S = nR \ln \frac{V_2}{V_1}$$

(for isothermal change)

$$\therefore \quad \Delta G = -nRT \ln \frac{V_2}{V_1}$$

Hence, during isothermal expansion Gibb's function decreases while during isothermal compression Gibb's function increases.

(ii) Isothermal and isobaric phase transitions :

At transition temperature, the stability (or Gibb's functions) of two phases are equal. Hence, there is no driving force for conversion of one phase into other. This means phase transitions are examples of reversible processes at transition temperature.

Now, for reversible, isothermal and isobaric change, $\Delta G = 0$

$\Rightarrow \Delta G = 0$, for phase transitions at transition temperature.

Thus, $\Delta G_{\text{vap}} = 0$ at boiling point :

$$\Rightarrow \Delta H_{\text{vap}} = T_b \Delta S_{\text{vap}}$$

$$\Rightarrow T_b = \frac{\Delta H_{\text{vap}}}{\Delta S_{\text{vap}}}$$

Also, $\Delta G_{\text{fusion}} = 0$ at melting point :

$$\Rightarrow \Delta H_{\text{fusion}} = T_f \Delta S_{\text{fusion}}$$

$$T_f = \frac{\Delta H_{\text{fusion}}}{\Delta S_{\text{fusion}}}$$

Ex.7 The enthalpy of vaporization of a liquid is 30 kJ mol^{-1} and entropy of vaporization is $75 \text{ J mol}^{-1} \text{ K}^{-1}$. The boiling point of the liquid at 1 atm is :

- (A) 250 K (B) 400 K (C) 450 K (D) 600 K

Ans. [B]

Sol. $T = \frac{\Delta H_{\text{vap}}}{\Delta S_{\text{vap}}} = \frac{30 \times 10^3}{75} = 400 \text{ K}$

Ex.8 At what minimum temperature would a given reaction become spontaneous if $\Delta H = +119 \text{ kJ}$ and $\Delta S = +263 \text{ J/K}$?

- (A) 452 K (B) 2210 K (C) 382 K (D) 2.21 K

Ans. [A]

Sol. $T = \frac{\Delta H}{\Delta S} = \frac{119 \times 10^3}{263} = 452.47 \text{ K}$

iii. $\Delta_r G$ for a chemical reaction.



The change in Gibb's function for a chemical reaction is change in ΔG when reactants react according to a given balanced chemical reaction with specified physical state of each reactant and product at given temperature and pressure.

$$\Delta_r G = cG_C + dG_D - aG_A - bG_B \quad \text{.....(i)}$$

Where G_A , G_B , G_C and G_D are molar Gibb's function of A, B, C and D respectively at given T and P.

also, $G_A = H_A - TS_A$

$$\left. \begin{aligned} G_B &= H_B - TS_B \\ G_C &= H_C - TS_C \\ G_D &= H_D - TS_D \end{aligned} \right\} \text{.....(ii)}$$

Substituting (ii) in (i)

$$\Delta_r G = (cH_C + dH_D - aH_A - bH_B) - T(cS_C + dS_D - aS_A - bS_B)$$

$$\Rightarrow \boxed{\Delta_r G = \Delta_r H - T\Delta_r S}$$

$(\Delta_r H)_{T,P}$	$(\Delta_r S)_{T,P}$	$(\Delta_r G)$	Remarks
- ve	+ ve	Always -ve	Reaction is spontaneous
+ ve	- ve	Always +ve	Reaction non-spontaneous
+ ve	+ ve	At low temperature, $\Delta G = +ve$	Non-spontaneous
		At high temperature, $\Delta G = -ve$	Spontaneous
- ve	- ve	At low temperature, - ve	Spontaneous
- ve	- ve	At high temperature, + ve	Non spontaneous

(iv) **Gibb's functions of pure substances :**

Consider a pure substance having a Gibb's function as follows :

$$G = H - TS = U + PV - TS$$

Let, the pressure and temperature are varied by infinitesimally small value :

$$dG = dU + PdV + VdP - TdS - SdT$$

As, $dU = dq - PdV$ and $TdS = dq$ [Assume only PV- work and reversible process.]

$$dG = VdP - SdT$$

(a) If pressure is varied keeping temperature constant -

$$dG = VdP \Rightarrow \left(\frac{dG}{dP} \right)_T = V$$

The physical significance of above relation is when pressure over a substance is increased, it's Gibb's function increases & the increase is proportional to molar volume. Since molar volume of gas, liquid and solid are in order, as follows :

$$V_{\text{Gas}} > V_{\text{Liquid}} > V_{\text{Solid}}$$

Hence, Gibb's function of gases increases most rapidly on increasing pressure.

That's why, gas phase becomes unstable at high pressure.

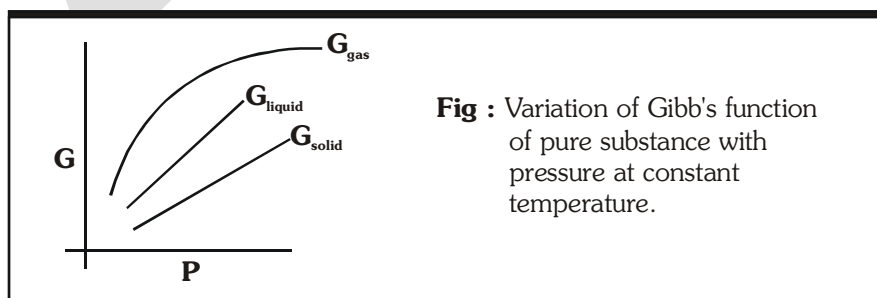


Fig : Variation of Gibb's function of pure substance with pressure at constant temperature.

(b) If temperature is changed keeping pressure constant -

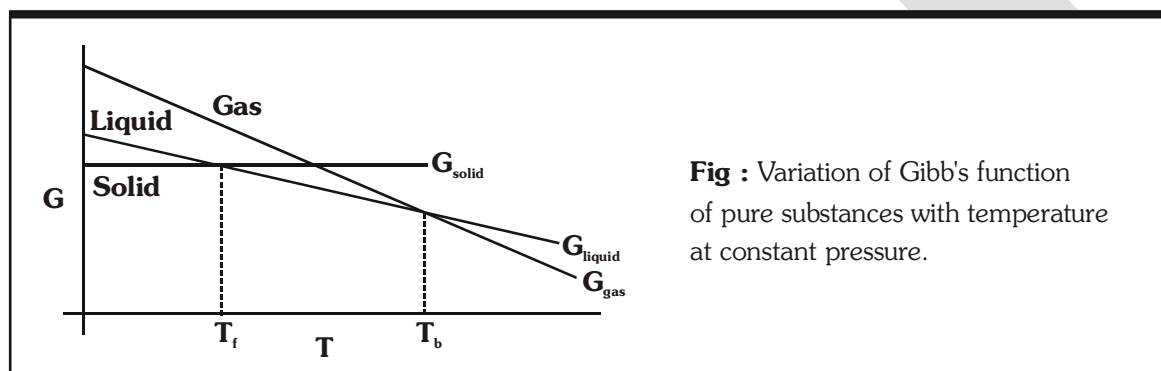
$$dG = -SdT \Rightarrow \left(\frac{dG}{dT} \right)_P = -S$$

Since entropy of pure substances are always positive, the slope of G vs T curve is negative. Also since,

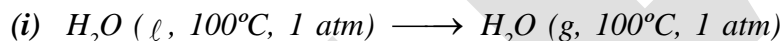
$$S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$$

\Rightarrow the slope is more negative for gas.

Thus, on increasing temperature, the Gibb's function of pure substances decreases, but this decrement is maximum for gaseous phase. Thus, gas phase acquire stability on increasing temperature.



Ex. 9. Calculate ΔG_m for the following process:



Sol. : (i) $\Delta G = 0$ (Equilibrium condition)



$$\Delta G_1 = 0$$

$$\Delta G_2 = nRT \cdot \ln \frac{P_2}{P_1} = 1 \times R \times 373 \times \ln \frac{0.5}{1} = -2149.5 \text{ J}$$

$$\therefore \Delta G = \Delta G_1 + \Delta G_2 = -2149.5 \text{ J}$$

8.3 APPLICATION OF GIBB'S ENERGY (AS MEASURE OF NON-PV WORK)

For a pure substance

$$dG = d(H - TS) = dH - TdS - SdT$$

also $dH = dU + PdV + VdP$

also $dU = dq - PdV - w_{\text{non-PV}}$

($w_{\text{non-PV}}$ = non-PV work done by system)

$$\Rightarrow dG = dq - PdV - w_{\text{non-PV}} + PdV + VdP - TdS - SdT$$

for a reversible change at constant T and P.

$dq = TdS$; and SdT and VdP term vanishes.

$$\Rightarrow dG = TdS - w_{\text{non-PV}} - TdS$$

$$(dG)_{T,P} = -w_{\text{non-PV}}$$

$$\Rightarrow \boxed{-(dG)_{T,P} = w_{\text{non-PV}}}$$

Thus decrease in Gibbs function at constant temperature and pressure is equal to maximum non-PV work obtainable from system.

9. Chemical equilibrium :

The state of chemical equilibrium is characterised by constant value of temperature, pressure and composition of a closed system. The state of equilibrium represent most stable state acquired by chemical system under given conditions.

The characteristics of state of equilibrium are :

- (i) The equilibrium is attained in closed system.
- (ii) At equilibrium, the chemical system is at minimum value of Gibbs function possible under given conditions.
- (iii) A state of equilibrium is attained spontaneously.
- (iv) At equilibrium, the rate of change of Gibbs function with progress of reaction under given conditions becomes zero $\Rightarrow \Delta_r G = 0$.
- (v) At state of equilibrium, the total Gibbs function of products becomes equal to total Gibbs function of reactants.

9.1 EQUILIBRIUM CONSTANT

Gas phase reactions :

Consider a reaction : $aA(g) + bB(g) \longrightarrow cC(g) + dD(g)$

Now molar Gibbs functions of A, B, C and D are given by :

$$G_A = G_A^\circ + RT \ln \left(\frac{P_A}{P_0} \right)$$

$$G_B = G_B^\circ + RT \ln \left(\frac{P_B}{P_0} \right)$$

$$G_C = G_C^\circ + RT \ln \left(\frac{P_C}{P_0} \right)$$

$$G_D = G_D^\circ + RT \ln \left(\frac{P_D}{P_0} \right)$$

Now, $\Delta_r G = cG_C + dG_D - aG_A - bG_B$

Substituting value of G_A , G_B , G_C and G_D in above equation :

$$\Delta_r G = (cG_C^\circ + dG_D^\circ - bG_B^\circ - aG_A^\circ) + RT \ln \left[\frac{\left(\frac{P_C}{P_0} \right)^c \left(\frac{P_D}{P_0} \right)^d}{\left(\frac{P_A}{P_0} \right)^a \left(\frac{P_B}{P_0} \right)^b} \right]$$

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q$$

Where, $Q = \left(\frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b} \right) \left(\frac{1}{P_0} \right)^{(c+d-a-b)}$

At equilibrium, $\Delta_r G = 0$ and $Q = K_p = \left(\frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b} \right) \left(\frac{1}{P_0} \right)^{\Delta n_g}$

$$\Delta_r G^\circ = -RT \ln K_p$$

Note : Q contains partial pressures at that moment but K_p contain partial pressures at equilibrium.

10. RELATIONSHIP BETWEEN, ΔG° AND EQUILIBRIUM CONSTANT

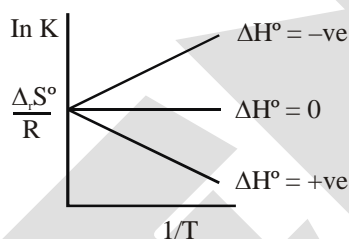
$$\Delta G^\circ = -RT \ln K_{eq}$$

$$\Delta H^\circ - T\Delta S^\circ = -RT \ln K_{eq}$$

$$\ln K_{eq} = \frac{-\Delta_r H^\circ}{RT} + \frac{\Delta_r S^\circ}{R}$$

$$\ln K_1 = \frac{\Delta_r S^\circ}{R} - \frac{\Delta_r H^\circ}{RT_1}$$

$$\ln K_2 = \frac{\Delta_r S^\circ}{R} - \frac{\Delta_r H^\circ}{RT_2}$$



[where K_1 & K_2 are values of K_p at temperature T_1 K & T_2 K respectively]

$$\ln \left(\frac{K_2}{K_1} \right) = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (\text{Van't Hoff's equation})$$

EXERCISE # 4

23. In a irreversible process taking place at constant T and P and in which only pressure-volume work is being done the change in Gibbs free energy (dG) and change in entropy (dS) satisfy the criteria:-
 (A) $(dS)_{V,E} = 0$, $(dG)_{T,P} = 0$ (B) $(dS)_{V,E} = 0$, $(dG)_{T,P} > 0$ [AIEEE-2003]
 (C) $(dS)_{V,E} < 0$, $(dG)_{T,P} < 0$ (D) $(dS)_{V,E} > 0$, $(dG)_{T,P} < 0$
24. The correct relationship between free energy change in a reaction and the corresponding equilibrium constant K_c is :- [AIEEE-2003]
 (A) $\Delta G^\circ = RT \ln K_c$ (B) $-\Delta G^\circ = RT \ln K_c$ (C) $\Delta G = RT \ln K_c$ (D) $-\Delta G = RT \ln K_c$
25. For the reaction at 298 K
 $A(g) + B(g) \rightleftharpoons C(g) + D(g)$
 $\Delta H^\circ = -29.8 \text{ kcal}$; $\Delta S^\circ = -0.1 \text{ kcal/K}$
 Calculate ΔG° and K .
26. The correct relationship between free energy change in a reaction and the corresponding equilibrium constant K is :-
 (A) $-\Delta G^\circ = RT \ln K$ (B) $\Delta G = RT \ln K$
 (C) $-\Delta G = RT \ln K$ (D) $\Delta G^\circ = RT \ln K$

ANSWER KEY**EXERCISE-1**

1. Ans. (i) irreversible, (ii) reversible, (iii) impossible
2. Ans.(A) 3. Ans.(B) 4. Ans.(C)

EXERCISE-2

5. Ans.(A)
6. Ans. (a) 2.1 cal/K , (b) 1.5 cal/K 7. Ans 819°C
8. Ans.(C)
9. Ans.
(A) (+ive) (B) (+ive) (C) ≈ 0 (D) (+ive)
(E) (+ive) (F) (-ive)
10. Ans.(C) 11. Ans.(C) 12. Ans.(D) 13. Ans.(B)
14. Ans.(C) 15. Ans.(A)

EXERCISE-3

16. Ans. -2873.1 kJ 17. Ans. (B) 18. Ans.(C) 19. Ans.(C)
20. Ans.(B) 21. Ans.(B) 22. Ans.(D)

EXERCISE-4

23. Ans.(D) 24. Ans.(B) 25. Ans. $\Delta G^\circ = 0$; $K = 1$
26. Ans.(A)

MISCELLANEOUS SOLVED QUESTION

1. When 1-pentyne(A) is treated with 4N alcoholic KOH at 175°C, it is converted slowly into an equilibrium mixture of 1.3% 1-pentyne (A), 95.2% 2-pentyne(B) & 3.5% of 1, 2-pentadiene (C). The equilibrium was maintained at 175°C. Calculate ΔG° for the following equilibria.



From the calculated value of ΔG_1° & ΔG_2° indicate the order of stability of A, B & C. Write a reasonable reaction mechanism sharing all intermediate leading to A, B & C. [JEE 2001]

2. Show that the reaction $\text{CO(g)} + \frac{1}{2} \text{O}_2\text{(g)} \longrightarrow \text{CO}_2\text{(g)}$ at 300 K is spontaneous and exothermic, when the standard entropy is $-0.094 \text{ kJ mol}^{-1} \text{ K}^{-1}$. The standard Gibbs free energies of formation for CO_2 and CO are -394.4 and $-137.2 \text{ kJ mol}^{-1}$, respectively. [JEE 2001]

3. $\text{N}_2\text{O}_4\text{(g)} \rightleftharpoons 2\text{NO}_2\text{(g)}$

This reaction is carried out at 298 K and 20 bar. 5 mol each of N_2O_4 and NO_2 are taken initially.

Given : $(\Delta G_f^\circ)_{\text{N}_2\text{O}_4} = 100 \text{ kJ mol}^{-1}$; $(\Delta G_f^\circ)_{\text{NO}_2} = 50 \text{ kJ mol}^{-1}$

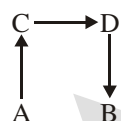
(i) Find ΔG for reaction at 298 K under given condition.

(ii) Find the direction in which the reaction proceeds to achieve equilibrium. [JEE 2004]

4. The enthalpy of vapourization of a liquid is 30 kJ mol^{-1} and entropy of vapourization is $75 \text{ J mol}^{-1} \text{ K}^{-1}$. The boiling point of the liquid at 1 atm is :- [JEE 2004]

(A) 250 K (B) 400 K (C) 450 K (D) 600 K

5. A process $A \longrightarrow B$ is difficult to occur directly instead it takes place in three successive steps.



$$\Delta S (A \longrightarrow C) = 50 \text{ e.u.}$$

$$\Delta S (C \longrightarrow D) = 30 \text{ e.u.}$$

$$\Delta S (B \longrightarrow D) = 20 \text{ e.u.}$$

[JEE 2006]

Where e.u. is entropy unit.

Then the entropy change for the process $\Delta S (A \longrightarrow B)$ is :-

(A) + 100 e.u. (B) - 60 e.u.

(C) - 100 e.u. (D) + 60 e.u.

6. For the process $\text{H}_2\text{O (l)} (1 \text{ bar}, 373 \text{ K}) \longrightarrow \text{H}_2\text{O (g)} (1 \text{ bar}, 373 \text{ K})$, the correct set of thermodynamic parameters is :- [JEE 2007]

(A) $\Delta G = 0$, $\Delta S = + \text{ve}$

(B) $\Delta G = 0$, $\Delta S = - \text{ve}$

(C) $\Delta G = + \text{ve}$, $\Delta S = 0$

(D) $\Delta G = - \text{ve}$, $\Delta S = + \text{ve}$

7. **Statement-1** : There is a natural asymmetry between converting work to heat and converting heat to work.

Statement-2 : No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work. [JEE 2008]

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
(C) Statement-1 is true, statement-2 is false.
(D) Statement-1 is false, statement-2 is true.

8. **Statement-1** : For every chemical reaction at equilibrium, standard Gibbs energy of reaction is zero.

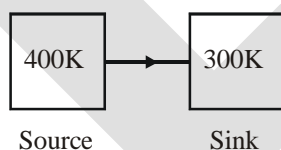
Statement-2 : At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs energy. [JEE 2008]

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
(C) Statement-1 is true, statement-2 is false.
(D) Statement-1 is false, statement-2 is true.

EXERCISE (S-I)

❑ Carnot Cycle

- The efficiency of a carnot cycle is $1/6$. On decreasing the temperature of the sink by 65°C , the efficiency increases to $1/3$. Calculate the temperature of source and sink.
- A carnot cycle has an efficiency of 40%. Its low temperature reservoir is at 9°C . What is the temperature of source ?
- A diatomic ideal gas is expanded isothermally to 32 times of its initial volume then it is cooled to restore to initial entropy at constant volume. Calculate ratio of initial temperature to final temperature
- One mole of an ideal monoatomic gas was taken through reversible isochoric heating from 100 K to 1000 K. Calculate ΔS_{system} , ΔS_{surr} and ΔS_{total}
 - when the process is carried out reversibly
 - when the process is carried out irreversibly (one step)
- 100 kJ heat is transferred from a large heat reservoir at 400 K to another large heat reservoir at 300 K. Suppose there is no change in temperature due to exchange of heat and combinedly source and sink from isolate system.

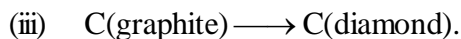
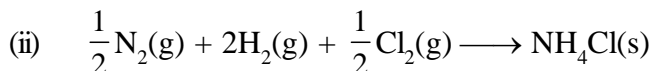
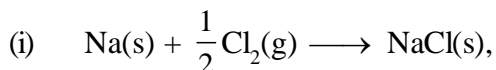


Find (a) ΔS_{source} , (b) ΔS_{sink} and (c) ΔS_{total} . Also comment on spontaneity of process.

- A system of 100 kg mass undergoes a process in which its specific entropy increases from $0.3 \text{ kJkg}^{-1}\text{K}^{-1}$ to $0.4 \text{ kJkg}^{-1}\text{K}^{-1}$. At the same time, the entropy of the surrounding decreases from $80 \text{ kJ}\text{K}^{-1}$ to $75 \text{ kJ}\text{K}^{-1}$. Find the $(\Delta S)_{\text{universe}}$ in kJK^{-1} .
- Calculate $(\Delta S)_{\text{universe}}$ (in cal/K) when 1kg water at 300K is brought into contact with a heat reservoir at 600K. Specific heat capacity of water is $1 \text{ cal/gm}^\circ\text{C}$. Assume no change in physical state of water. ($\ln 2 = 0.7$)
- 1 mole of ideal monoatomic gas is heated by supplying 5 kJ heat from a reservoir maintained at 400 K from 300 K to 400 K. In the process volume of gas increased from 1 L to 10 L. Find ΔS_{total} (in J/K-mol) in the process

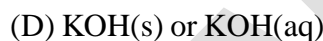
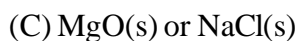
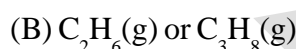
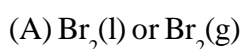
Use : $\ln \left(\frac{4}{3} \right) = 0.3$, $\ln 10 = 2.3$, $R = 8.3 \text{ J/K-mol}$ and $\ln x = 2.3 \log x$

9. Calculate ΔS_r° at 298K of



The values of S° of Na, Cl_2 , NaCl, NH_4Cl , N_2 , H_2 diamond & graphite are 51, 223, 72, 95, 192, 131, 2.43 & 5.69 $\text{JK}^{-1}\text{mol}^{-1}$ respectively.

10. Identify the substance in each of the following pairs of samples that has the higher entropy?



□ Gibbs's Function

11. Calculate the ΔG° change at 300 K for the reaction;

$\text{Br}_2(\text{l}) + \text{Cl}_2(\text{g}) \longrightarrow 2\text{BrCl(g)}.$ For the reaction $\Delta H^\circ = 29.3 \text{ kJ}$ & the standard entropies of $\text{Br}_2(\text{l})$, $\text{Cl}_2(\text{g})$ & BrCl(g) at the 300 K are 150, 220, 240 $\text{J mol}^{-1}\text{K}^{-1}$ respectively.

12. The standard entropies of $\text{H}_2(\text{g})$ and H(g) are 130 and 115 $\text{J mol}^{-1}\text{K}^{-1}$ respectively at 300K. Using the data given below calculate the bond energy of H_2 (in kJ/mol) :-



13. 5 mole $\text{H}_2\text{O}(\text{l})$ at 373K and 1 atm is converted into $\text{H}_2\text{O(g)}$ at 373K and 5 atm. Calculate ΔG for this process. [Given : $R = 2\text{Cal/K-mol}$, $\ln 5 = 1.6$]

14. Calculate ΔG (in bar-L) when a definite mass of a monoatomic ideal gas at 1 bar & 27°C is expanded adiabatically against vacuum from 10 L to 20 L ($\ln 2 = 0.7$)

15. Find $(\Delta S)_{\text{universe}}$ (in Joule/mole/K) at 1 bar for a chemical reaction at 300 K if $\Delta H_{300\text{K}}^\circ = 75 \text{ kJ/mol}$ $\Delta S_{300\text{K}}^\circ = 300 \text{ J/K}$

16. A liquid freezes into a solid ($\Delta H = -1000 \text{ J/mole}$) at 200 K and 1 atm, (it's normal melting point).

(i) What is the value of ΔG at 200 K ?

(ii) What is the ΔS value at 200 K ?

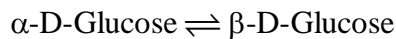
(iii) Will the freezing be spontaneous at 150 K and 1 atm ? Calculate ΔS_{total} , assuming ΔS and ΔH do not depend on temperature.

(iv) What is the value of ΔG at 250 K and 1 atm ? Assuming ΔS and ΔH do not depend on temperature.

(Assume ΔS and ΔH do not depend on temperature)

☐ Thermodynamic and equilibrium constant

17. α -D Glucose undergoes mutarotation to β -D-Glucose in aqueous solution. If at 300K there is 60% conversion. Calculate ΔG° of the reaction. ($\ln 2 = 0.7$, $\ln 3 = 1.1$)



18. The equilibrium constant of the reaction $2\text{C}_3\text{H}_6(\text{g}) \rightleftharpoons \text{C}_2\text{H}_4(\text{g}) + \text{C}_4\text{H}_8(\text{g})$ is found to fit the expression

$$\ln K = -1.04 - \frac{1088\text{K}}{T}$$

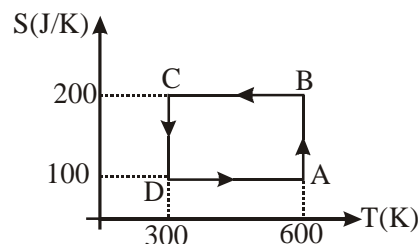
Calculate the standard reaction enthalpy and entropy at 400 K.

19. For the reaction $\text{SO}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g})$; $\Delta H^\circ_{300} = -95 \text{ kJ/mole}$,
 $\Delta S^\circ_{300} = -95.0 \text{ J/K mole}$. Find the value of $\ln k_p$ for this reaction at 300 K.

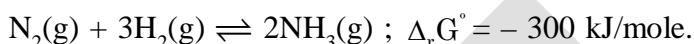
EXERCISE-(S-II)

1. From the given T-S diagram of a reversible carnot engine, find

- (i) work delivered by engine in one cycle
 (ii) heat taken from the source in each cycle.
 (iii) ΔS_{sink} in each cycle.



2. At 300 K, $\Delta H^{\circ}_{\text{combustion}}(\text{sucrose}) = -5000 \text{ kJ/mol}$ & $\Delta G^{\circ}_{\text{combustion}}(\text{sucrose}) = -6000 \text{ kJ/mol}$. Estimate additional non-PV work that is obtained by raising temperature to 309 K. Assume $\Delta_r C_p = 0$ for this temperature change.
3. The K_p for reaction $A + B \rightleftharpoons C + D$ is 2.0 at 27°C and 8.0 at 127°C . Determine the standard free energy change of this reaction at each temperature and ΔH° for the reaction over this range of temperature ($\ln 2 = 0.7$) ?
4. Pressure of 10 moles of an ideal gas is changed from 2 atm to 1 atm against constant external pressure without change in temperature. If surrounding temperature (300 K) and pressure (1 atm) always remains constant then calculate total entropy change ($\Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$) for given process.
5. What is $\Delta_r G$ for synthesis of ammonia at 300 K at following sets of partial pressure :



[Take $R = \frac{25}{3} \text{ J/K mole}$, $\ln 2 = 0.7$, $\ln 3 = 1.1$, $\ln 5 = 1.6$]

Gas	N_2	H_2	NH_3
Pressure (atm)	1	3	0.02

6. $2\text{A}(\text{s}) \rightleftharpoons \text{B}(\text{g}) + 2\text{C}(\text{g}) + 3\text{D}(\text{g})$

Total pressure developed in a closed container by decomposition of A at equilibrium is 12 bar at 727°C . Calculate $|\Delta G^{\circ}|$ (in kcal) of the reaction at 727°C ($R = 2 \text{ cal/mole-K}$, $\ln 2 = 0.7$, $\ln 3 = 1.1$)

7. Find $\Delta G(\text{J/mol})$ for the reaction at 300 kPa & 27°C when all gases are in stoichiometric ratio of moles.
 $\text{N}_2\text{O}_4(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$ [$\ln 2 = 0.7$]

Given: $\Delta G_f^{\circ}(\text{N}_2\text{O}_4) = 100 \text{ kJ/mol}$

$\Delta G_f^{\circ}(\text{NO}_2) = 50 \text{ kJ/mol}$

$R = 8 \text{ J/mol-K}$

8. Oxygen is heated from 300 to 600 K at a constant pressure of 1 bar. What is the increases in molar entropy ? The molar heat capacity (in $\text{JK}^{-1} \text{mol}^{-1}$) for the O_2 is (Given : $\ln 2 = 0.7$)

$$C_{P,m} = 10 + 10^{-2}T$$

9. Calculate the molar entropy of a substance at 600 K and 1 bar using the following data.

(i) Heat capacity of solid from 0K to normal melting point 200 K

$$C_{p,m}(s) = 0.035 T \text{ JK}^{-1}\text{mol}^{-1}.$$

(ii) Enthalpy of fusion = 7.5 kJ mol^{-1} ,

(iii) Enthalpy of vaporisation = 30 kJ mol^{-1} ,

(iv) Heat capacity of liquid from 200K to normal boiling point 300K

$$C_{p,m}(\ell) = 60 + 0.016T \text{ JK}^{-1}\text{mol}^{-1}.$$

(v) Heat capacity of gas from 300K to 600K at 1 atm

$$C_{p,m}(g) = 50.0 \text{ JK}^{-1}\text{mol}^{-1}.$$

10. For a reaction : $2A(s) + B(g) \longrightarrow 3C(l)$, standard entropy change of reaction is 2 kJ/mol-K and standard enthalpy of combustion of $A(s)$, $B(g)$ and $C(l)$ are -100 , -60 -285 kJ/mol respectively, then find the maximum useful work that can be obtained at 27°C and 1 bar pressure from the reaction (in kJ/mol).

EXERCISE (O-I)

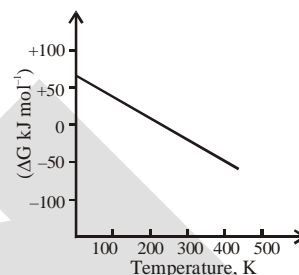
- A reversible heat engine A (based on Carnot cycle) absorbs heat from a reservoir at 1000 K and rejects heat to a reservoir at T_2 . A second reversible engine B (based on Carnot cycle) absorbs the same amount of heat as rejected by the engine A, from the reservoir at T_2 and rejects energy to a reservoir at 360 K.
If the efficiencies of engines A and B are the same then the temperature T_2 is :-
(A) 680 K (B) 640 K (C) 600 K (D) 670 K
- Which of the following is incorrect for a closed system in which an irreversible process is occurring?
(A) $Q_{\text{sys}} + Q_{\text{surr}} = 0$ (B) $W_{\text{sys}} + W_{\text{surr}} = 0$
(C) $\Delta U_{\text{sys}} + \Delta U_{\text{surr}} = 0$ (D) $\Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$
- For conversion $\text{C}(\text{graphite}) \rightarrow \text{C}(\text{Diamond})$, the ΔS is :-
(A) Zero (B) Positive
(C) Negative (D) Can not be predicted
- Considering entropy (S) as a thermodynamic parameter, the criteria for the spontaneity of any process is :-
(A) $\Delta S_{\text{system}} - \Delta S_{\text{surroundings}} > 0$ (B) $\Delta S_{\text{system}} > 0$ only
(C) $\Delta S_{\text{surroundings}} > 0$ only (D) $\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$
- If $\Delta H_{\text{vaporisation}}$ of substance X(l) (molar mass = 30 g/mol) is 300 J/g at its boiling point 300 K, then molar entropy change for reversible condensation process is :-
(A) 30 J/mol.K (B) -300 J/mol.K (C) -30 J/mol.K (D) -10 J/mol.K
- For 1 mole of an ideal monoatomic gas on moving from one state to other, the temperature is doubled but pressure becomes $\sqrt{2}$ times. Then entropy change in the process will be
(R = 2 Cal/mol.K)
(A) $R \ln 2$ (B) $2R \ln 2$ (C) $3R \ln 2$ (D) $\frac{R}{2} \ln 2$
- If S° for H_2 , Cl_2 and HCl are 0.13, 0.22 and 0.19 $\text{kJ K}^{-1} \text{mol}^{-1}$ respectively. The total change in standard entropy for the reaction, $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$ is :
(A) $30 \text{ JK}^{-1} \text{mol}^{-1}$ (B) $40 \text{ JK}^{-1} \text{mol}^{-1}$ (C) $60 \text{ JK}^{-1} \text{mol}^{-1}$ (D) $20 \text{ JK}^{-1} \text{mol}^{-1}$
- For a perfectly crystalline solid $C_{p,m} = aT^3$, where a is constant. If $C_{p,m}$ is 0.42 J/K-mol at 10 K, molar entropy at 10 K is
(A) 0.42 J/K-mol (B) 0.14 J/K-mol (C) 4.2 J/K-mol (D) Zero
- Identify the correct statement regarding entropy.
(A) At absolute zero, the entropy of perfectly crystalline substance is taken to be +ve
(B) At absolute zero, entropy of perfectly crystalline substance is taken to be zero.
(C) At 0 °C, the entropy of a perfectly crystalline substance is taken to be zero.
(D) At absolute zero, the entropy of all crystalline substances is taken to be zero.

10. In which of the following reactions do you expect to have a decrease in entropy?

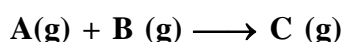
- (A) $\text{Fe(s)} \longrightarrow \text{Fe(l)}$
 (B) $2 \text{Fe(s)} + 3/2 \text{O}_2\text{(g)} \longrightarrow \text{Fe}_2\text{O}_3\text{(s)}$
 (C) $\text{HF(l)} \longrightarrow \text{HF(g)}$
 (D) $2 \text{H}_2\text{O}_2\text{(l)} \longrightarrow 2 \text{H}_2\text{O(l)} + \text{O}_2\text{(g)}$

11. What can be concluded about the values of ΔH and ΔS from this graph?

- (A) $\Delta H > 0, \Delta S > 0$ (B) $\Delta H > 0, \Delta S < 0$
 (C) $\Delta H < 0, \Delta S > 0$ (D) $\Delta H < 0, \Delta S < 0$



12. For the reaction at 300 K



$$\Delta U = -3.0 \text{ kcal} ; \Delta S = -10.0 \text{ cal/K}$$

value of ΔG is ?

- (A) -600 cal (B) -6600 cal (C) -6000 cal (D) none

13. For the reaction that taking place at certain temperature $\text{NH}_4\text{HS(s)} \rightleftharpoons \text{NH}_3\text{(g)} + \text{H}_2\text{S(g)}$, if equilibrium pressure is X bar, then $\Delta_r G^\circ$ would be :-

- (A) $-2 RT \ln X$ (B) $-RT (\ln X - \ln 2)$
 (C) $-2 RT (\ln X - \ln 2)$ (D) $-0.5 RT (\ln X - \ln 2)$

14. What is the free energy change (ΔG) when 1.0 mole of water at 100°C and 1 atm pressure is converted into steam at 100°C and 1 atm pressure ?

- (A) 80 cal (B) 540 cal (C) 620 cal (D) zero

15. What is the free energy change (ΔG) when 1.0 mole of water at 100°C and 1 atm pressure is converted into steam at 100°C and 2 atm pressure ?

- (A) Zero (B) 540 cal (C) 517.13 cal (D) 510 cal

16. If $\Delta G^\circ > 0$ for a gaseous reaction then :

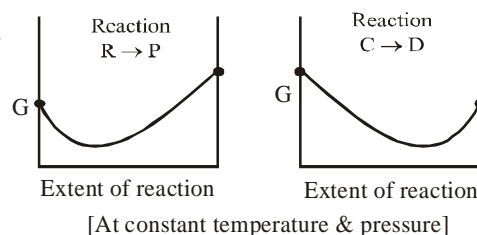
- (A) $K_p > 1$
 (B) $K_p < 1$
 (C) The products predominate in the equilibrium mixture
 (D) Mole of product must be less than mole of reactant

17. Heat liberated for an ideal gas undergoing reversible isothermal process is 1200 cal at 300 K. What will be Gibb's free energy change for the process ?

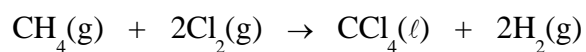
- (A) 1200 cal (B) -1200 cal (C) 400 cal (D) -400 cal

18. With the help of given curves select the correct statement.

- (A) C will partially convert into D.
 (B) R will not convert into P
 (C) R will be completely converted into P.
 (D) C will be completely converted in D.



19. Evaluate ΔS° for the reaction below at 25°C .



Given :

	$\text{CH}_4(\text{g})$	$\text{Cl}_2(\text{g})$	$\text{CCl}_4(\ell)$	$\text{H}_2(\text{g})$
ΔH_f° (kJ/mol)	-74.81	0	-135.4	0
ΔG_f° (kJ/mol)	-50.75	0	-65.27	0
(A) -360 J/K	(B) -66.9 J/K	(C) -155 J/K	(D) -487 J/K	

20. All of the following have $\Delta G_f^\circ = 0$, except -

(A) $\text{O}_2(\text{g})$ (B) $\text{Br}_2(\text{g})$ (C) $\text{H}_2(\text{g})$ (D) $\text{Ca}(\text{s})$

EXERCISE (O-II)

Single correct :

1. When two equal sized pieces of the same metal at different temperatures T_h (hot piece) and T_c (cold piece) are brought into thermal contact and isolated from its surrounding. The total change in entropy of system is given by ? Suppose heat capacity of each piece is C .

(A) $C \ln \frac{T_c + T_h}{2T_c}$ (B) $C \ln \frac{T_2}{T_1}$ (C) $C \ln \frac{(T_c + T_h)^2}{2T_h \cdot T_c}$ (D) $C \ln \frac{(T_c + T_h)^2}{4T_h \cdot T_c}$

2. The change in entropy of 2 moles of an ideal gas upon isothermal expansion at 243.6 K from 20 litre until the pressure becomes 1 atm, is :-

(A) 1.385 cal/K (B) - 1.2 cal/K (C) 1.2 cal/K (D) 2.77 cal/K

3. For the hypothetical reaction, $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$, $\Delta_r G$ and $\Delta_r S$ are 20 kJ/mole and $-20 \text{ JK}^{-1} \text{ mol}^{-1}$ respectively at 200 K. If $\Delta_r C_p$ is $20 \text{ JK}^{-1} \text{ mol}^{-1}$ then $\Delta_r H$ at 400 K is :-

(A) 20 kJ/mole (B) 7.98 kJ/mole (C) 28 kJ/mole (D) 16 kJ/mole

4. A mole of steam is condensed at 100°C , the water is cooled to 0°C and frozen to ice. What is the difference in entropies of the ice and steam ? The heats of vaporization and fusion are 540 cal gm^{-1} and 80 cal gm^{-1} respectively. Use the average heat capacity of liquid water as $1 \text{ cal gm}^{-1} \text{ degree}^{-1}$.

(A) $18 \left(\frac{80}{373} + \frac{540}{373} + \ln \frac{373}{273} \right)$ (B) $18 \left(\frac{80}{273} + \frac{540}{373} + \ln \frac{373}{273} \right)$

(C) $18 \left(\frac{80}{273} + \frac{540}{373} + \ln \frac{273}{373} \right)$ (D) $18 \left(\frac{80}{273} + \frac{540}{373} + 100 \right)$

5. The value of ΔG_f° of gaseous mercury is 38 kJ/mole. At what total external pressure mercury start boiling at 27°C . ($R \cdot \ln 10 = 19 \text{ J/K-mol}$)

(A) $10^{-6.67}$ (B) $10^{-1.67}$ (C) $10^{-13.33}$ (D) $10^{-3.33}$

6. If molar internal energy for a gas in a closed rigid vessel given by

$$U = a + bT + cT^2$$

find the entropy change (in J/K) at constant volume when 1 mol of gas are heated from 200 K to 400K. [Given : $a = 20 \text{ J/mol}$; $b = 10 \text{ J/K-mol}$; $c = 2 \times 10^{-2} \text{ J/K}^2\text{-mol}$] ($\ln 2 = 0.7$)

(A) 15 (B) 30 (C) 60 (D) 9.78

7. Statement - 1 : When process $\text{H}_2\text{O}(s) \rightleftharpoons \text{H}_2\text{O}(l)$, reaches equilibrium in a closed system at constant temperature and pressure, Gibb's function of $\text{H}_2\text{O}(s)$ & $\text{H}_2\text{O}(l)$ become same.

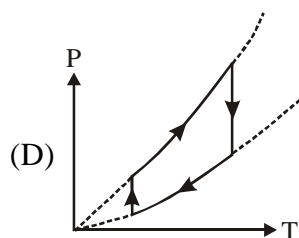
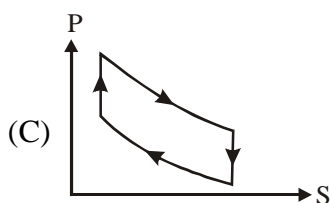
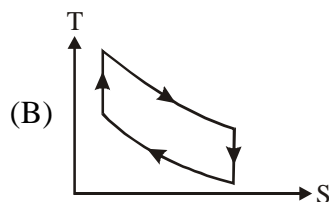
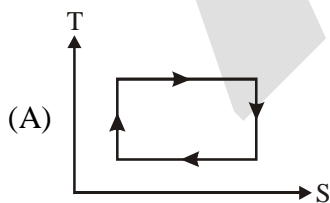
Statement - 2 : For reversible phase change at constant temperature & pressure, change in Gibb's free energy will be zero.

- (A) Statement-1 is true, statement- 2 is true and statement- 2 is correct explanation for statement-1.
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
 (C) Statement-1 is true, statement-2 is false
 (D) Statement-1 is false, statement-2 is true.

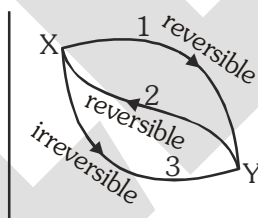
8. Statement-1 : Absolute entropy of an ion in aqueous solution at 298 K may be negative.
Statement -2 : Absolute entropy at 298 K of any substance can never be negative.
(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
(C) Statement-1 is true, statement-2 is false
(D) Statement-1 is false, statement-2 is true.
9. **Statement-1** : Net heat absorbed in a cyclic process must be always equal to net work done by the system in the cyclic process.
Statement-2 : Internal energy of system is a function of state.
(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
(C) Statement-1 is true, statement-2 is false.
(D) Statement-1 is false, statement-2 is true.
10. **Statement-1** : Entropy change in reversible adiabatic expansion of an ideal gas is zero.
Statement-2 : The increase in entropy due to volume increase just compensate the decrease in entropy due to fall in temperature.
(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
(C) Statement-1 is true, statement-2 is false.
(D) Statement-1 is false, statement-2 is true.

MORE THAN ONE MAY BE CORRECT :

11. Select the correct statement(s).
(A) In a reversible process, ΔG is always zero in a closed system.
(B) In a reversible process, ΔS_{univ} is always zero in a closed system.
(C) In a reversible process, ΔS_{sys} is always zero in a closed system.
(D) In a reversible process, ΔS_{sys} is always zero in an isolated system.
12. Which of the following statement (s) is/ are correct ?
(A) The quantities E, H and G have the same dimension
(B) Gibb's free energy of 10 gm ice at 0°C and 1.0 atm is less than the Gibb's free energy of 10 gm water at 0°C and 1 atm.
(C) $\Delta S_{\text{sys}} = 0$ for every adiabatic process in a closed system.
(D) For every reversible process in a closed system, $\Delta S_{\text{sys}} = \frac{\Delta H_{\text{sys}}}{T}$
13. Which of the following represents the carnot cycle-



14. The normal boiling point of a liquid 'A' is 350 K. ΔH_{vap} at normal boiling point is 35 kJ/mole. Pick out the correct statement(s). (Assume ΔH_{vap} to be independent of pressure).
- (A) $\Delta S_{\text{vaporisation}} > 100 \text{ J/K mole}$ at 350 K and 0.5 atm
(B) $\Delta S_{\text{vaporisation}} < 100 \text{ J/K mole}$ at 350 K and 0.5 atm
(C) $\Delta S_{\text{vaporisation}} < 100 \text{ J/K mole}$ at 350 K and 2 atm
(D) $\Delta S_{\text{vaporisation}} = 100 \text{ J/K mole}$ at 350 K and 2 atm
15. In isothermal ideal gas compression :
- (A) w is + ve (B) ΔH is zero (C) ΔS_{gas} is + ve (D) ΔG is + ve
16. Which of the following statement (s) is/are false :
- (A) $\Delta_r S$ for $\frac{1}{2}\text{N}_2(\text{g}) \longrightarrow \text{N}(\text{g})$ is positive
(B) ΔG_{system} is always zero for a reversible process in a closed system
(C) ΔG° for an ideal gas is a function of temperature and pressure
(D) Entropy of a closed system is always maximized at equilibrium
17. Which of the following processes are spontaneous ?
- (A) Burning of fossil fuel
(B) Decomposition of water into H_2 and O_2 gas at room temperature
(C) Spreading of perfume in a room
(D) Diffusion of gas from high pressure to low pressure
18. Suppose a system make a transition from state X to state Y.



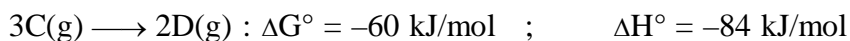
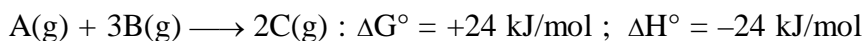
Given : $\Delta S_{\text{xy}} = 10 \text{ J/K}$

- (A) The state Y is more disordered than state X.
- (B) ΔS_{XY} for path 1 and 3 is same.
- (C) $\Delta S_{YX} = -10 \text{ J/K}$
- (D) The transition $X \rightarrow Y$ must be spontaneous.
- 19.** In which of the following processes involving an ideal gas, entropy of system remains constant?
- (A) Reversible isothermal expansion (B) Irreversible adiabatic expansion
- (C) Reversible adiabatic expansion (D) Free expansion
- 20.** In which of the following process involving ideal gas, entropy of surrounding remains constant?
- (A) Reversible isobaric heating (B) Reversible adiabatic expansion
- (C) Irreversible adiabatic compression (D) Free expansion

Paragraph for Question 21 to 22

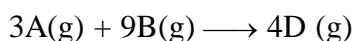
The reactions whose ΔG° are positive can not take place under standard state conditions. However another reaction whose ΔG° is negative can be coupled with the former type of reaction to give overall spontaneous process.

Consider the given reactions whose ΔG° at 300 K are provided to answer following questions.



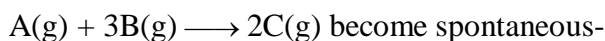
All data at 300 K temperature.

21. What is ΔS° at 300 K of reaction (in J/Kmole) :



- (A) -640 (B) -480 (C) +640 (D) -240

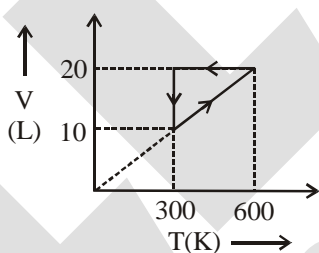
22. Assuming ΔH° and ΔS° do not vary with temperature. At what temperature reaction



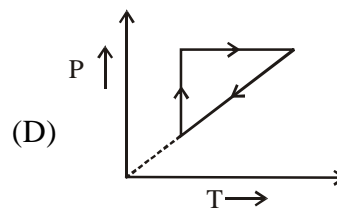
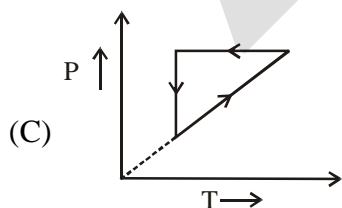
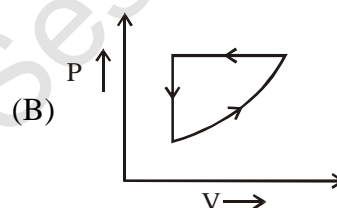
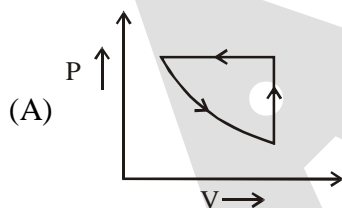
- (A) 6250 K (B) 625 K (C) 150 K (D) 1000 K

Paragraph for Q.23 to Q.24

One mol of ideal monoatomic gas undergo the state change as shown in the following graph ($\ln 2 = 0.7$)



23. Correct graph for the process in paragraph is -



24. Efficiency of the cycle will be -

- (A) 50% (B) 25% (C) 13.63% (D) 12%

Table type question :

Column-I	Column-II	Column-III
(A) Combustion of butane gas at S.T.P.	(P) Entropy change of universe constant	(I) Low temperature conditions favourable
(B) Dissolution of sodium chloride in water at STP	(Q) Entropy change of system positive	(II) More spontaneous at high temperature
(C) Adding carbon dioxide gas to water to form carbonated water at high pressure and 298K	(R) Enthalpy change of system negative	(III) High pressure condition favourable
(D) Vaporisation of liquid water at 1 atm and 373K	(S) Entropy change of universe positive	(IV) More spontaneous at low pressure

25. Which of following option is incorrect -

- (A) A – S – I (B) B – Q – IV (C) C – R – I (D) D – P – IV

26. In column-I (A) if the reaction was carried at 400 K which option would be correct -

- (A) A – P – II (B) A – Q – III (C) A – S – IV (D) A – R – III

27. In column-I (D), if vaporisation is carried out at 15 atm which option is correct -

- (A) D – P – IV (B) D – S – II (C) D – R – I (D) D – Q – II

MATCH THE LIST :

28. Match the Column :

Column-I	Column-II
(P) $\text{H}_2\text{O} (\ell, 1 \text{ atm}, 363 \text{ K}) \rightarrow \text{H}_2\text{O} (\text{g}, 1 \text{ atm}, 363 \text{ K})$	(1) $\Delta_r S > 0$
(Q) $\text{H}_2\text{O} (\text{s}, 1 \text{ atm}, 373 \text{ K}) \rightarrow \text{H}_2\text{O} (\text{g}, 1 \text{ atm}, 373 \text{ K})$	(2) $\Delta_r G > 0$
(R) $\text{H}_2\text{O} (\ell, 1 \text{ atm}, 273 \text{ K}) \rightarrow \text{H}_2\text{O} (\text{s}, 1 \text{ atm}, 273 \text{ K})$	(3) $\Delta_r H < 0$
(S) $\text{H}_2\text{O} (\text{s}, 1 \text{ atm}, 353 \text{ K}) \rightarrow \text{H}_2\text{O} (\ell, 1 \text{ atm}, 353 \text{ K})$	(4) $\Delta_r U > 0$

Code:

	P	Q	R	S
(A)	2	4	1	3
(B)	4	2	3	1
(C)	2	1	3	4
(D)	4	3	1	2

MATCH THE COLUMN :

29. Column-I

- (A) Reversible adiabatic compression
(B) Reversible vaporisation
(C) Adiabatic free expansion of ideal gas in vacuum
(D) Dissociation of $\text{CaCO}_3(\text{s}) \longrightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$

Column-II

- (P) $\Delta S_{\text{system}} > 0$
(Q) $\Delta S_{\text{system}} < 0$
(R) $\Delta S_{\text{surrounding}} < 0$
(S) $\Delta S_{\text{surrounding}} = 0$

30. Column-I

(Related to process)

- (A) Fusion at melting point
(B) Vapourisation at boiling point
(C) Condensation at triple point
(D) Melting at normal boiling point

Column-II

(Related to system)

- (P) $\Delta G = 0$
(Q) $\Delta G < 0$
(R) $\Delta S > 0$
(S) $\Delta H \approx \Delta U$

EXERCISE (J-MAIN)

1. The entropy change involved in the isothermal reversible expansion of 2 moles of an ideal gas from a volume of 10 dm³ to a volume of 100 dm³ at 27°C is :- [AIEEE-2011]

- (1) 32.3 J mol⁻¹ K⁻¹ (2) 42.3 J mol⁻¹ K⁻¹
(3) 38.3 J mol⁻¹ K⁻¹ (4) 35.8 J mol⁻¹ K⁻¹

2. The incorrect expression among the following is :-

- (1) $K = e^{-\Delta G^\circ/RT}$ [AIEEE-2012]

(2) $\frac{\Delta G_{\text{system}}}{\Delta S_{\text{total}}} = -T$

(3) In isothermal process, $W_{\text{reversible}} = -nRT \ln \frac{V_f}{V_i}$

(4) $\ln K = \frac{\Delta H^\circ - T\Delta S^\circ}{RT}$

3. The entropy (S°) of the following substances are : [JEE-MAINS-(online) 2014]

CH₄ (g) 186.2 J K⁻¹ mol⁻¹

O₂ (g) 205.0 J K⁻¹ mol⁻¹

CO₂ (g) 213.6 J K⁻¹ mol⁻¹

H₂O (l) 69.9 J K⁻¹ mol⁻¹

The entropy change (ΔS°) for the reaction



- (1) -312.5 JK⁻¹ mol⁻¹ (2) -37.6 JK⁻¹ mol⁻¹
(3) -108.1 JK⁻¹ mol⁻¹ (4) -242.8 JK⁻¹ mol⁻¹

4. The molar heat capacity (C_p) of CD₂O is 10 cal at 1000 K. The change in entropy associated with cooling of 32 g of CD₂O vapour from 1000 K to 100 K at constant pressure will be

(D = deuterium, at. mass = 2u) [JEE-MAINS-(online) 2014]

- (1) -23.03 cal deg⁻¹ (2) 2.303 cal deg⁻¹ (3) 23.03 cal deg⁻¹ (4) -2.303 cal deg⁻¹

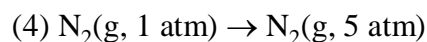
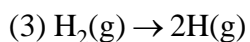
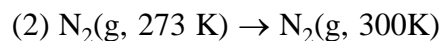
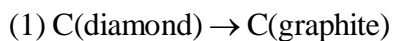
5. Δ_fG° at 500 K for substance 'S' in liquid state and gaseous state are +100.7 kcal mol⁻¹ and +103 kcal mol⁻¹, respectively. Vapour pressure of liquid 'S' at 500 K is approximately equal to :

(R = 2 cal K⁻¹ mol⁻¹) - [JEE-MAINS-(online) 2018]

- (1) 0.1 atm (2) 10 atm (3) 100 atm (4) 1 atm

6. For which of the following processes, ΔS is negative?

[JEE-MAINS-(online) 2018]



7. At 320 K, a gas A_2 is 20% dissociated to $\text{A}(\text{g})$. The standard free energy change at 320 K and 1 atm in J mol^{-1} is approximately :

[JEE-MAINS-(online) 2018]

($R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$; $\ln 2 = 0.693$; $\ln 3 = 1.098$)

(1) 4281

(2) 4763

(3) 2068

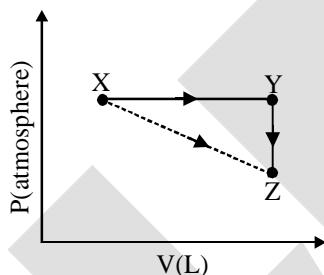
(4) 1844

EXERCISE (J-ADVANCE)

1. Match the transformations in **Column-I** with appropriate option in **Column-II** [JEE 2011]

Column-I	Column-II
(A) $\text{CO}_2(\text{s}) \rightarrow \text{CO}_2(\text{g})$	(p) phase transition
(B) $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$	(q) allotropic change
(C) $2\text{H}\cdot \rightarrow \text{H}_2(\text{g})$	(r) ΔH is positive
(D) $\text{P}_{(\text{white, solid})} \rightarrow \text{P}_{(\text{red, solid})}$	(s) ΔS is positive
	(t) ΔS is negative

2. For an ideal gas, consider only P-V work in going from an initial state X to the final state Z. The final state Z can be reached by either of the two paths shown in the figure. Which of the following choice(s) is (are) correct ? [take ΔS as change in entropy and w as work done] [JEE 2012]



- (A) $\Delta S_{x \rightarrow z} = \Delta S_{x \rightarrow y} + \Delta S_{y \rightarrow z}$ (B) $W_{x \rightarrow z} = W_{x \rightarrow y} + W_{y \rightarrow z}$
 (C) $W_{x \rightarrow y \rightarrow z} = W_{x \rightarrow y}$ (D) $\Delta S_{x \rightarrow y \rightarrow z} = \Delta S_{x \rightarrow y}$

3. For the process [JEE 2014]



at $T = 100^\circ\text{C}$ and 1 atmosphere pressure, the correct choice is

- (A) $\Delta S_{\text{system}} > 0$ and $\Delta S_{\text{surroundings}} > 0$ (B) $\Delta S_{\text{system}} > 0$ and $\Delta S_{\text{surroundings}} < 0$
 (C) $\Delta S_{\text{system}} < 0$ and $\Delta S_{\text{surroundings}} > 0$ (D) $\Delta S_{\text{system}} < 0$ and $\Delta S_{\text{surroundings}} < 0$

4. Match the thermodynamic processes given under Column-I with the expressions given under Column-II. [JEE 2015]

Column - I	Column - II
(A) Freezing of water at 273 K and 1 atm	(P) $q = 0$
(B) Expansion of 1 mol of an ideal gas into a vacuum under isolated conditions	(Q) $w = 0$
(C) Mixing of equal volumes of two ideal gases at constant temperature and pressure in an isolated container	(R) $\Delta S_{\text{sys}} < 0$
(D) Reversible heating of $\text{H}_2(\text{g})$ at 1 atm from 300 K to 600 K followed by reversible cooling to 300 K at 1 atm	(S) $\Delta U = 0$
	(T) $\Delta G = 0$

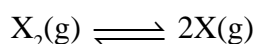
5. One mole of an ideal gas at 300 K in thermal contact with surroundings expands isothermally from 1.0 L to 2.0 L against a constant pressure of 3.0 atm. In this process, the change in entropy of surroundings (ΔS_{surr}) in J K^{-1} is - [JEE 2016]

(1 L atm = 101.3 J)

- (A) 5.763 (B) 1.013 (C) -1.013 (D) -5.763

Paragraph for Q.6 & Q.7

Thermal decomposition of gaseous X_2 to gaseous X at 298 K takes place according to the following equation : [JEE 2016]



The standard reaction Gibbs energy, $\Delta_r G^\circ$, of this reaction is positive. At the start of the reaction, there is one mole of X_2 and no X. As the reaction proceeds, the number of moles of X formed is given by β . Thus, $\beta_{\text{equilibrium}}$ is the number of moles of X formed at equilibrium. The reaction is carried out at a constant total pressure of 2 bar. Consider the gases to behave ideally.

(Given : $R = 0.083 \text{ L bar K}^{-1} \text{ mol}^{-1}$)

6. The equilibrium constant K_p for this reaction at 298 K, in terms of $\beta_{\text{equilibrium}}$, is
- (A) $\frac{8\beta_{\text{equilibrium}}^2}{2-\beta_{\text{equilibrium}}}$ (B) $\frac{8\beta_{\text{equilibrium}}^2}{4-\beta_{\text{equilibrium}}^2}$ (C) $\frac{4\beta_{\text{equilibrium}}^2}{2-\beta_{\text{equilibrium}}}$ (D) $\frac{4\beta_{\text{equilibrium}}^2}{4-\beta_{\text{equilibrium}}^2}$
7. The **INCORRECT** statement among the following for this reaction is
- (A) Decrease in the total pressure will result in formation of more moles of gaseous X
- (B) At the start of the reaction, dissociation of gaseous X_2 takes place spontaneously
- (C) $\beta_{\text{equilibrium}} = 0.7$
- (D) $K_c < 1$
8. The standard state Gibbs free energies of formation of C(graphite) and C(diamond) at $T = 298 \text{ K}$ are [JEE 2017]

$$\Delta_f G^\circ [\text{C(graphite)}] = 0 \text{ kJ mol}^{-1}$$

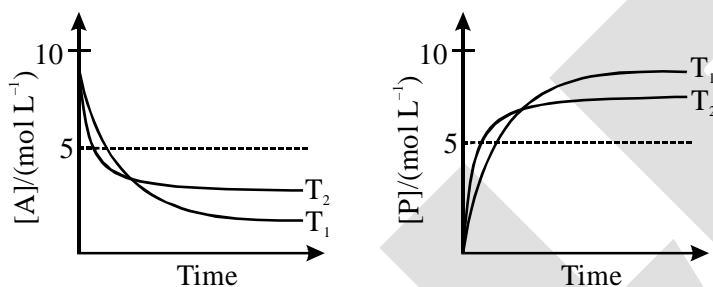
$$\Delta_f G^\circ [\text{C(diamond)}] = 2.9 \text{ kJ mol}^{-1}$$

The standard state means that the pressure should be 1 bar, and substance should be pure at a given temperature. The conversion of graphite [C(graphite)] to diamond [C(diamond)] reduces its volume by $2 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$. If C(graphite) is converted to C(diamond) isothermally at $T = 298 \text{ K}$, the pressure at which C(graphite) is in equilibrium with C(diamond), is

[Useful information : $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$; $1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$; $1 \text{ bar} = 10^5 \text{ Pa}$]

- (A) 14501 bar (B) 29001 bar (C) 58001 bar (D) 1405 bar

9. For a reaction taking place in a container in equilibrium with its surroundings, the effect of temperature on its equilibrium constant K in terms of change in entropy is described by
- With increase in temperature, the value of K for exothermic reaction decreases because the entropy change of the system is positive
 - With increase in temperature, the value of K for endothermic reaction increases because unfavourable change in entropy of the surroundings decreases
 - With increase in temperature, the value of K for exothermic reaction decreases because favourable change in entropy of the surroundings decreases
 - With increase in temperature, the value of K for endothermic reaction increases because the entropy change of the system negative
10. For a reaction, $A \rightleftharpoons P$, the plots of $[A]$ and $[P]$ with time at temperatures T_1 and T_2 are given below. [JEE 2018]



If $T_2 > T_1$, the correct statement(s) is (are)

(Assume ΔH^θ and ΔS^θ are independent of temperature and ratio of $\ln K$ at T_1 to $\ln K$ at T_2 is greater than T_2/T_1 . Here H , S , G and K are enthalpy, entropy, Gibbs energy and equilibrium constant, respectively.)

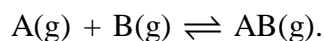
- $\Delta H^\theta < 0$, $\Delta S^\theta < 0$
 - $\Delta G^\theta < 0$, $\Delta H^\theta > 0$
 - $\Delta G^\theta < 0$, $\Delta S^\theta < 0$
 - $\Delta G^\theta < 0$, $\Delta S^\theta > 0$
11. The surface of copper gets tarnished by the formation of copper oxide. N_2 gas was passed to prevent the oxide formation during heating of copper at 1250 K. However, the N_2 gas contains 1 mole % of water vapour as impurity. The water vapour oxidises copper as per the reaction given below
- $$2\text{Cu(s)} + \text{H}_2\text{O(g)} \rightarrow \text{Cu}_2\text{O(s)} + \text{H}_2\text{(g)}$$
- p_{H_2} is the minimum partial pressure of H_2 (in bar) needed to prevent the oxidation at 1250 K. The value of $\ln(p_{\text{H}_2})$ is ____.

(Given : total pressure = 1 bar, R (universal gas constant) = $8 \text{ JK}^{-1} \text{ mol}^{-1}$, $\ln(10) = 2.3$. Cu(s) and $\text{Cu}_2\text{O(s)}$ are mutually immiscible.

At 1250 K : $2\text{Cu(s)} + 1/2\text{O}_2(\text{g}) \rightarrow \text{Cu}_2\text{O(s)}$; $\Delta G^\theta = -78,000 \text{ J mol}^{-1}$

$\text{H}_2(\text{g}) + 1/2\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O(g)}$; $\Delta G^\theta = -1,78,000 \text{ J mol}^{-1}$; G is the Gibbs energy) [JEE 2018]

12. Consider the following reversible reaction, [JEE 2018]



The activation energy of the backward reaction exceeds that of the forward reaction by $2RT$ (in J mol^{-1}). If the pre-exponential factor of the forward reaction is 4 times that of the reverse reaction, the absolute value of ΔG^θ (in J mol^{-1}) for the reaction at 300 K is ____.

(Given ; $\ln(2) = 0.7$, $RT = 2500 \text{ J mol}^{-1}$ at 300 K and G is the Gibbs energy)

ANSWER KEY

EXERCISE (S-I)

1. Ans. 117°C , 52°C
2. Ans. 197°C
3. Ans. (4)
4. Ans. (i) $\Delta S_{\text{syst}} = 28.72\text{J/K}$; $\Delta S_{\text{surr}} = -28.72\text{ J/K}$; $\Delta S_{\text{total}} = 0$
(ii) $\Delta S_{\text{sys}} = 28.72\text{J/K}$; $\Delta S_{\text{surr}} = -11.22\text{ J/K}$, $\Delta S_{\text{total}} = 17.50\text{ J/K}$
5. Ans. (a) -250 J/K (b) 333.33 J/K (c) $+83.33\text{ J/K}$. Process is spontaneous.
6. Ans.(5)
7. Ans (200)
8. Ans. 10.325
9. Ans. (i) -90.5 (ii) -374.5 (iii) -3.26 (all in $\text{J mol}^{-1}\text{ K}^{-1}$)
10. Ans. [A] - II ; [B] - II ; [C] - II ; [D] - II
11. Ans. -3.7 kJ
11. Ans 436 kJ
13. Ans. 5.968 kcal
14. Ans.(-7)
15. Ans. (50)
16. Ans.
(i) $\Delta G = 0$
(ii) $\Delta S = -5\text{ J/mole.K}$
(iii) $\Delta S_{\text{total}} = +1.66\text{ J/ mole. K}$; process is spontaneous
(iv) $\Delta S_{\text{total}} = -\text{J/mole. K} = \Delta G = +250\text{ J/mole. K}$]
17. Ans. -997.68 J/mol
18. Ans. $\Delta H^{\circ} = 9.04\text{ kJ/mol}$; $\Delta S^{\circ} = -8.64\text{ J/mol}^{-1}\text{ K}^{-1}$
19. Ans. 26.7

EXERCISE-(S-II)

1. Ans. (i) 30 kJ (ii) 60 kJ (iii) 100 J/K
2. Ans. 30 kJ/mole
3. Ans. -1745.94 J/mol ; -6983.76 J/mol and 13.97 kJ/mol
4. Ans. (16 J/K)
5. Ans. (-57.75 kJ/ mol)
6. Ans. (17.8)
7. Ans.(3360)
8. Ans 10 J/K
9. Ans. $205.08\text{ JK}^{-1}\text{mol}^{-1}$
10. Ans.(5)

EXERCISE (O-I)

- | | | | |
|-------------|--------------|--------------|-------------|
| 1. Ans.(C) | 2. Ans.(D) | 3. Ans.(C) | 4. Ans.(D) |
| 5. Ans.(C) | 6. Ans.(B) | 7. Ans.(A) | 8. Ans.(B) |
| 9. Ans.(B) | 10. Ans.(B) | 11. Ans.(A) | 12. Ans.(A) |
| 13. Ans.(C) | 14. Ans.(D) | 15. Ans.(C) | 16. Ans.(B) |
| 17. Ans.(A) | 18. Ans. (A) | 19. Ans. (C) | 20. Ans.(B) |

EXERCISE (O-II)

- | | | | |
|--|-----------------|-----------------|-----------------|
| 1. Ans.(D) | 2. Ans.(D) | 3. Ans.(A) | 4. Ans.(B) |
| 5. Ans.(A) | 6. Ans.(A) | 7. Ans.(A) | 8. Ans.(C) |
| 9. Ans.(A) | 10. Ans.(A) | 11. Ans.(B,D) | 12. Ans.(A) |
| 13. Ans. (A,C,D) | 14. Ans.(A,C) | 15. Ans.(A,B,D) | 16. Ans.(B,C,D) |
| 17. Ans.[A,C,D] | 18. Ans.[A,B,C] | 19. Ans.[C] | 20. Ans.[B,C,D] |
| 21. Ans.(A) | 22. Ans.(C) | 23. Ans.(D) | 24. Ans.(D) |
| 25. Ans.(B) | 26. Ans.(C) | 27. Ans.(D) | 28. Ans.(C) |
| 29. Ans. (A) - S ; (B) - P,R ; (C) - P, S (D) - P, R | | | |
| 30. Ans. (A) - P,S,R ; (B) - P,R ; (C) - P (D) - Q, R, S | | | |

EXERCISE (J-MAIN)

- | | | | |
|------------|------------|------------|------------|
| 1. Ans.(3) | 2. Ans.(4) | 3. Ans.(4) | 4. Ans.(1) |
| 5. Ans.(1) | 6. Ans.(4) | 7. Ans.(2) | |

EXERCISE (J-ADVANCE)

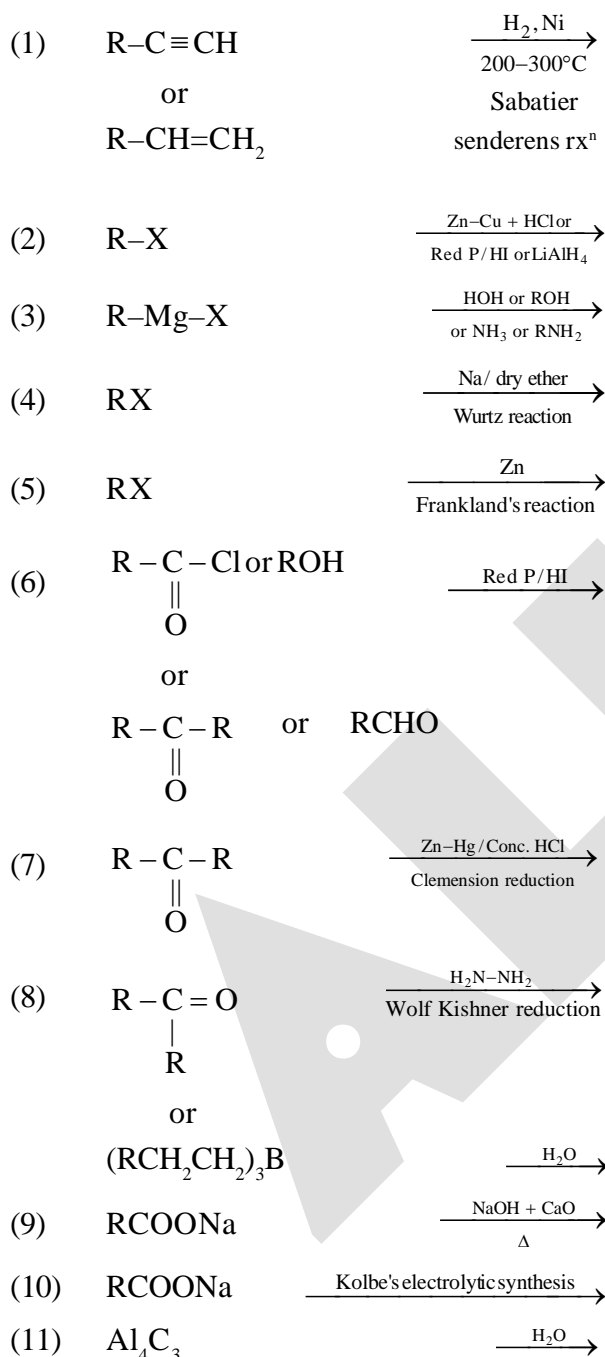
- | | | | |
|---|---------------|-----------------|----------------|
| 1. Ans.(A)→(p, r, s) ; (B)→(r, s) ; (C)→(t) ; (D)→(p, q, t) | | | |
| 2. Ans.(A), (C) | 3. Ans. (B) | | |
| 4. Ans. (A) → R, T ; (B) → P, Q, S ; (C) → P, Q, S ; (D) → P, Q, S, T | | | |
| 5. Ans. (C) | 6. Ans.(B) | 7. Ans.(C) | 8. Ans.(A) |
| 9. Ans.(BC) | 10. Ans.(A,C) | 11. Ans.(-14.6) | 12. Ans.(8500) |

HYDROCARBON

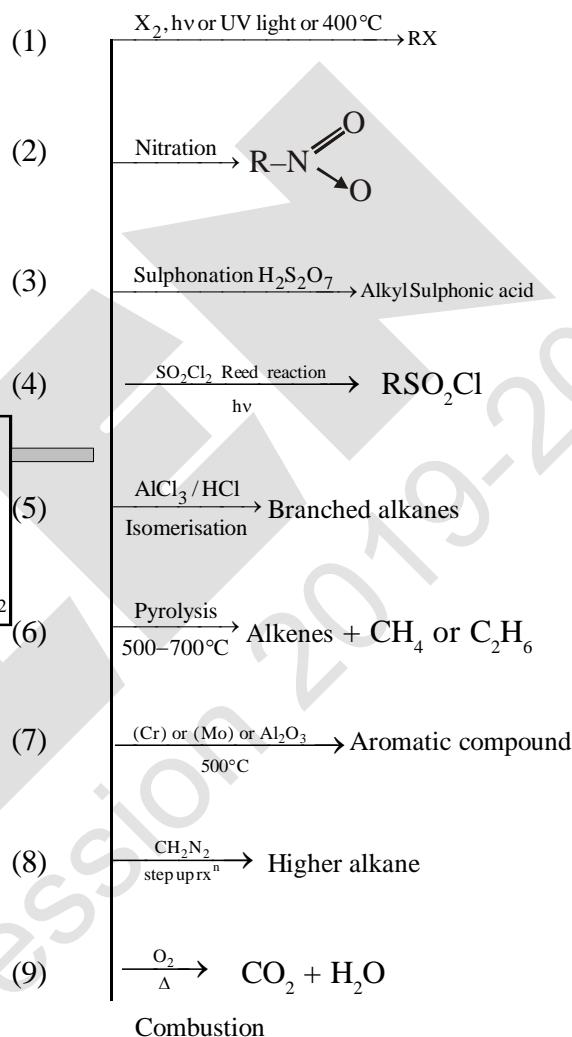
REACTION CHART FOR ALKANES

GMP

GR

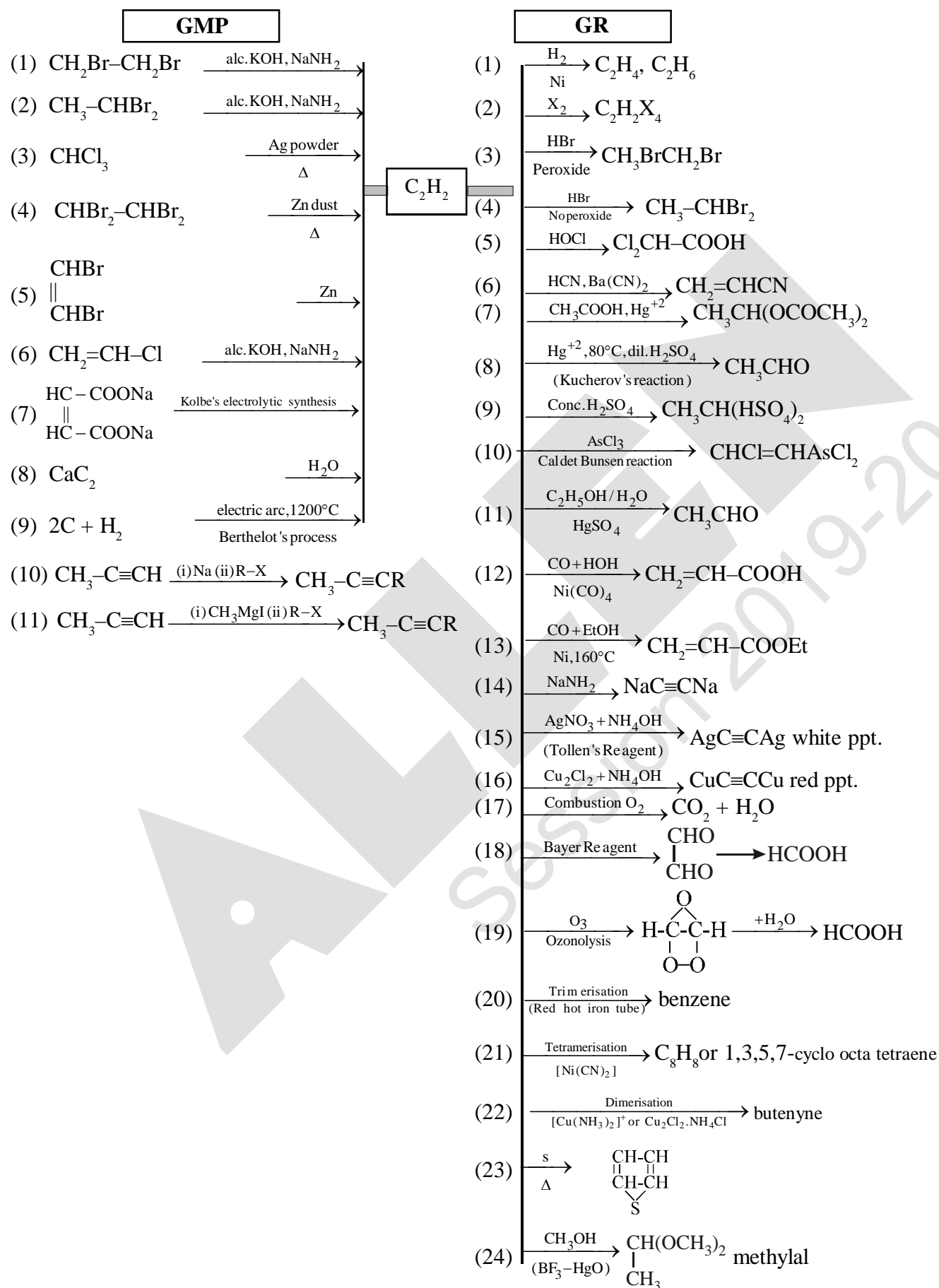


R-H
or
R-R
or
 C_nH_{2n+2}



GR

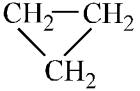
REACTION CHART FOR ALKYNES



EXERCISE # I

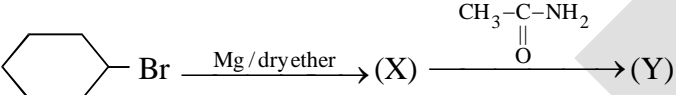
1. During the preparation of ethane by Kolbe's electrolytic method using inert electrodes the pH of the electrolyte –
- (A) Increases progressively as the reaction proceeds
 (B) Decreases progressively as the reaction proceeds
 (C) Remains constant throughout the reaction
 (D) May decrease if the concentration of the electrolyte is not very high

2. $\text{BrCH}_2\text{--CH}_2\text{--CH}_2\text{Br}$ reacts with Na in the presence of ether at 100°C to produce –

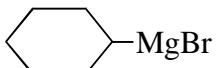


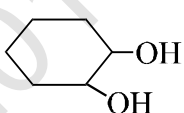
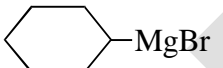

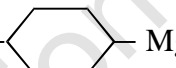
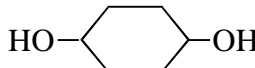
- (A) $\text{BrCH}_2\text{--CH=CH}_2$ (B) $\text{CH}_2\text{=C=CH}_2$ (C)  (D) All of these

3. How many products will be formed excluding stereo when cis-1,3,5-trimethyl cyclohexene reacts with NBS?

- (A) 3 (B) 4 (C) 5 (D) 6

4. 

The structures of (X) and (Y) respectively are

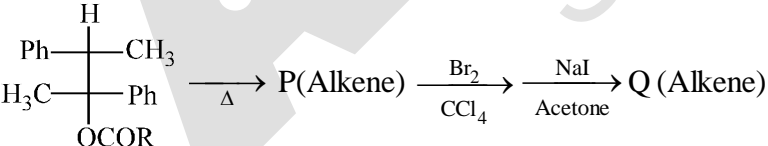
- (A)  ;  (B)  ; 
 (C)  ;  (D)  ; 

5. When n-butane is heated in the presence of AlCl_3/HCl it will be converted into –

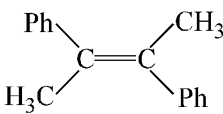
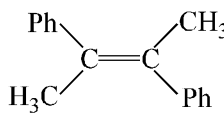
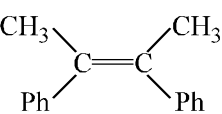
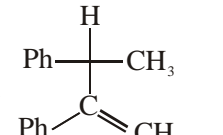
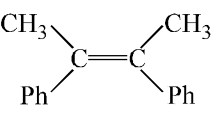
- (A) Ethane (B) Propane (C) Butene (D) Isobutane

6. How many dibromo derivatives are formed when bromine is added to 3-Methyl Cyclohexene in 1,2-dichloroethane.

- (A) 2 (B) 3 (C) 4 (D) 6

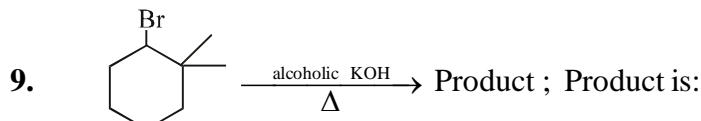
7. 

Alkene (P) & (Q) respectively are

- (A) Both  (B)  , 
 (C) Both  (D) Both 

8. Anti-Markownikoff's addition of HBr is not observed in –

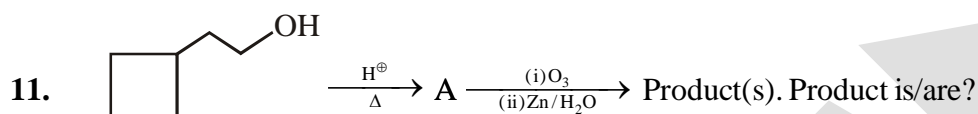
- (A) Propene (B) But-2-ene (C) But-1-ene (D) Pent-2-ene



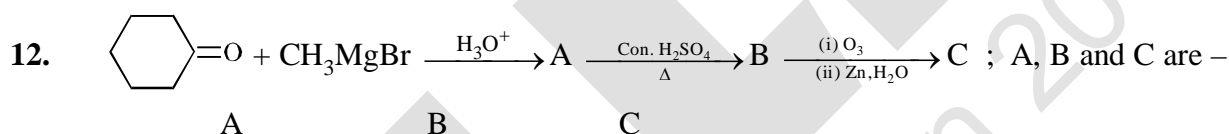
- (A)  (B)  (C)  (D) 

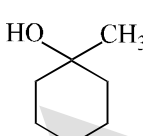
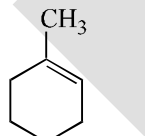
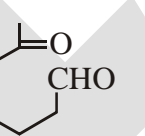
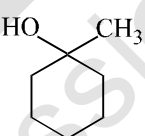
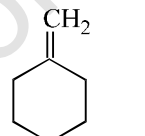
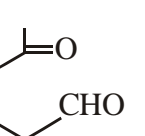
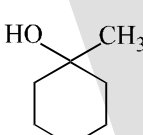
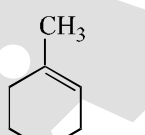
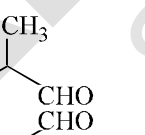
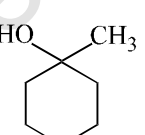
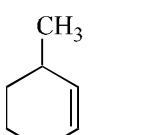
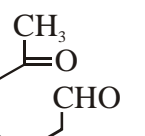
10. Which is expected to react most readily with bromine –

- (A) $\text{CH}_3\text{CH}_2\text{CH}_3$ (B) $\text{CH}_2=\text{CH}_2$ (C) $\text{CH}\equiv\text{CH}$ (D) $\text{CH}_3-\text{CH}=\text{CH}_2$

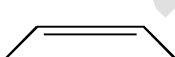
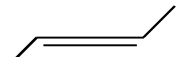
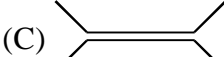
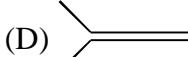


- (A)  + HCHO (B) 
(C)  + CH_3CHO (D) 



- (A)    (B)   
(C)    (D)   

13. Which has least heat of hydrogenation –

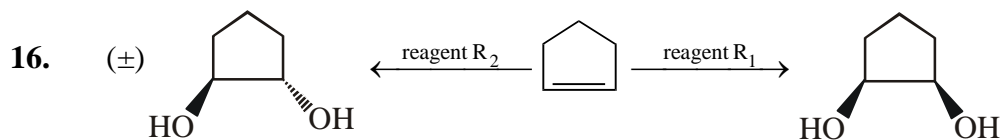
- (A)  (B)  (C)  (D) 

14. For the ionic reaction of hydrochloric acid with the following alkenes, predict the correct sequence of reactivity as measured by reaction rates:

- (I) $\text{ClCH}=\text{CH}_2$ (II) $(\text{CH}_3)_2\text{C}=\text{CH}_2$ (III) $\text{OHC}\cdot\text{CH}=\text{CH}_2$ (IV) $(\text{NC})_2\text{C}=\text{C}(\text{CN})_2$
(A) $\text{IV} > \text{I} > \text{III} > \text{II}$ (B) $\text{I} > \text{IV} > \text{II} > \text{III}$ (C) $\text{III} > \text{II} > \text{IV} > \text{I}$ (D) $\text{II} > \text{I} > \text{III} > \text{IV}$

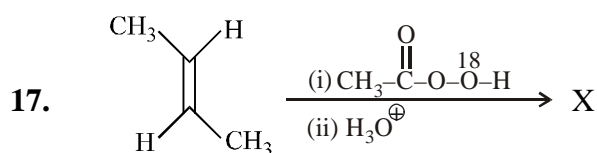
15. $\text{CH}_3\text{-CH=CH-CH}_3 \xrightarrow{\text{X}}$ Product is Y (non-resolvable) then X can be –
cis

(A) Br_2 water (B) HCO_3H
(C) Cold alkaline KMnO_4 (D) all of the above

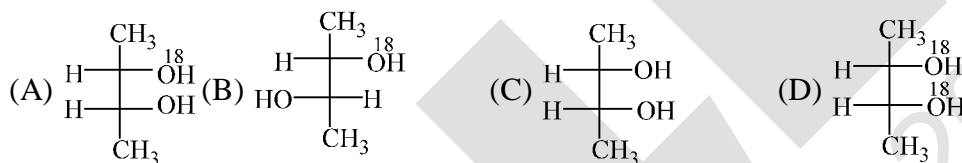


R_1 and R_2 respectively are –

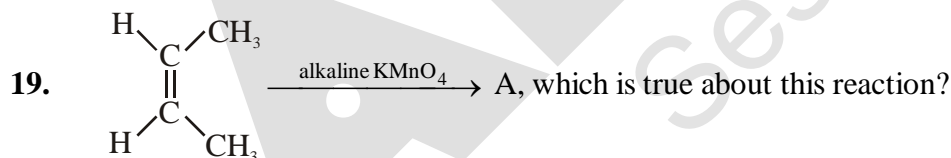
(A) Cold alkaline KMnO_4 , $\text{OsO}_4/\text{H}_2\text{O}_2$ (B) Cold alkaline KMnO_4 , HCO_3H
(C) Cold alkaline KMnO_4 , $\text{CH}_3\text{-O-O-CH}_3$ (D) $\text{C}_6\text{H}_5\text{CO}_3\text{H}$, HCO_3H



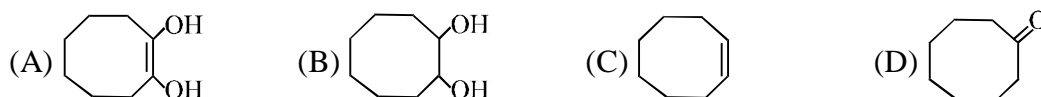
The probable structure of 'X' is

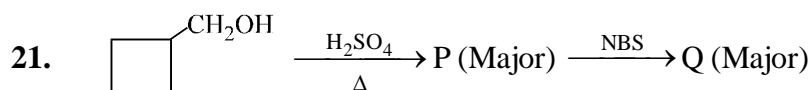


18. Which alkene on heating with alkaline KMnO_4 solution gives acetone and a gas, which turns lime water milky –
(A) 2-Methyl-2-butene (B) Isobutylene
(C) 1-Butene (D) 2-Butene

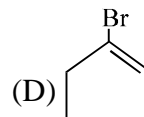
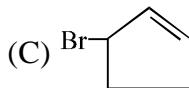
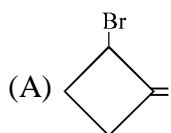


- (A) A is meso 2, 3-butanediol formed by *syn* addition
(B) A is meso 2, 3-butanediol formed by *anti* addition
(C) A is a racemic mixture of d and l, 2, 3-butanediol formed by anti addition
(D) A is a racemic mixture of d and l 2,3-butanediol formed by *syn* addition
20. The reaction of cyclooctyne with HgSO_4 in the presence of a H_2SO_4 gives

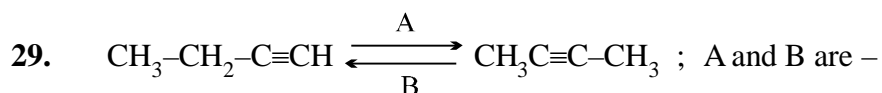




The structure of Q is



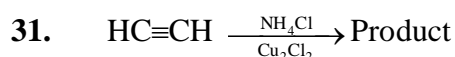
22. Mixture of one mole each of ethene and propyne on reaction with Na will form H_2 gas at S.T.P. –
 (A) 22.4 L (B) 11.2 L (C) 33.6 L (D) 44.8 L
23. Acetylene may be prepared using Kolbe's electrolytic method employing –
 (A) Pot. acetate (B) Pot. succinate (C) Pot. fumarate (D) None of these
24. $B \xleftarrow{\text{Lindlar}} R-C\equiv C-R \xrightarrow{Na/NH_3} A$
 A and B are geometrical isomers –
 (A) A is trans, B is cis (B) A and B both are cis
 (C) A and B both are trans (D) A is cis, B is trans
25. A mixture of CH_4 , C_2H_4 and C_2H_2 gaseous are passed through a Wolf bottle containing ammonical cuprous chloride. The gas coming out is
 (A) Methane (B) Acetylene
 (C) Mixture of methane and ethylene (D) original mixture
26. $B \xleftarrow[H_2O_2, OH^-]{BH_3, THF} CH_3-C\equiv CH \xrightarrow{HgSO_4/H_2SO_4} A$
 A and B are –
 (A) CH_3CH_2CHO , $CH_3-C(=O)-CH_3$ (B) $CH_3-C(=O)-CH_3$, CH_3CH_2CHO
 (C) CH_3CH_2CHO (both) (D) $CH_3-C(=O)-CH_3$ (both)
27. Which of the following reagents cannot be used to locate the position of triple bond in $CH_3-C\equiv C-CH_3$
 (A) Br_2/CCl_4 (B) O_3/H_2O (C) Cu_2Cl_2/NH_4OH (D) $KMnO_4/H^+$
28. In the presence of strong bases, triple bonds will migrate within carbon skeletons by the
 (A) removal of protons (B) addition of protons
 (C) removal and readdition of protons (D) addition and removal of protons.



- (A) alcoholic KOH and NaNH_2 (B) NaNH_2 and alcoholic KOH
(C) NaNH_2 and Lindlar catalyst (D) Lindlar and NaNH_2 catalyst

30. If a mixture of iso-octane (70%) & n-heptane (30%) is present in sample. The octane number of this sample is :

- (A) 40 (B) 70 (C) 30 (D) 85



Product is –

- (A) $\text{Cu--C}\equiv\text{C--Cu}$ (B) $\text{H}_2\text{C=CH--C}\equiv\text{CH}$ (C) $\text{HC}\equiv\text{C--Cu}$ (D) $\text{Cu--C}\equiv\text{C--NH}_4$

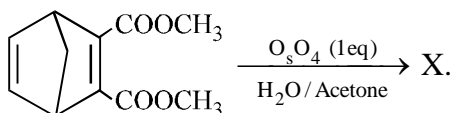
32. Which of the following process is not good for the preparation of open chain alkane having odd number of carbons :

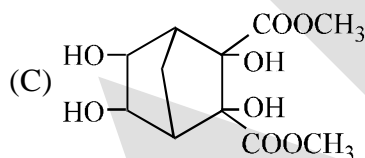
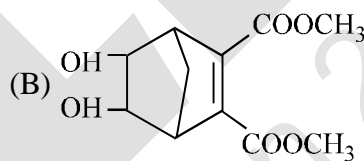
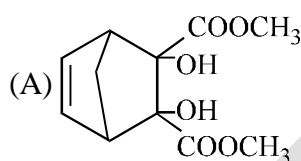
- (A) Wurtz process (B) Kolbe electrolysis
(C) Corey house synthesis (D) Both (A) & (B)

EXERCISE # II

- How many moles of O_2 required for complete combustion of one mole of propane –
(A) 7 (B) 5 (C) 16 (D) 10
- How much volume of air will be needed for complete combustion of 10 lit. of ethane –
(Assuming that approx 20% O_2 is present in air)
(A) 135 lit. (B) 35 lit. (C) 175 lit. (D) 205 lit.

- $CH_3CH=CH_2 \xrightarrow[H_2O_2/OH^-]{B_2D_6}$ product X ; X is –
(A) $CH_3-\underset{\substack{| \\ OH}}{CH}-CH_2D$ (B) $CH_3-\underset{\substack{| \\ D}}{CH}-CH_2OH$
(C) $CH_3-\underset{\substack{| \\ OD}}{CH}-CH_3$ (D) none is correct

-  Identify 'X'.



(D) Reaction will not occur

- Aqueous solution of potassium propanoate is electrolysed. Possible organic products are:
(A) n-Butane (B) $C_2H_5COOC_2H_5$
(C) CH_3-CH_3 (D) $CH_2=CH_2$

- $Ph-\overset{\overset{O}{||}}{C}-CH_3 \xrightarrow{A} Ph-CH_2-CH_3$

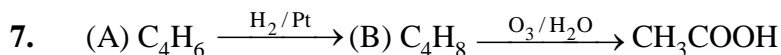
A could be:

(A) NH_2NH_2 , glycol/ OH^- , Δ

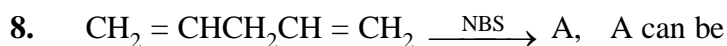
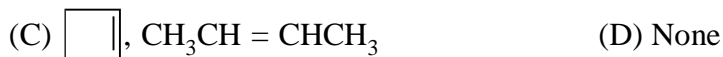
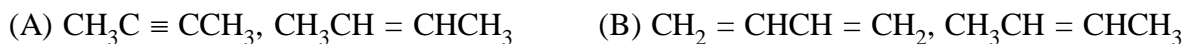
(B) $Na(Hg)/conc. HCl$

(C) Red P/HI

(D) CH_2-CH_2 ; Raney Ni, H_2 , Δ
 $\begin{array}{cc} | & | \\ SH & SH \end{array}$



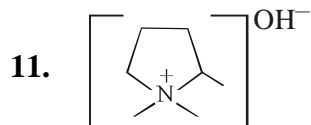
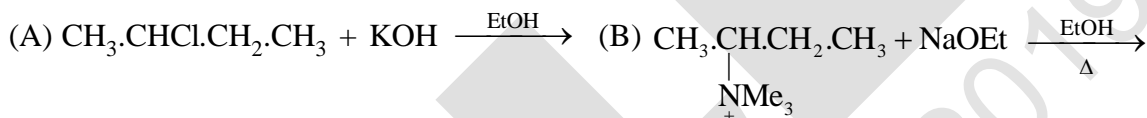
Hence A and B are



9. An alkene on ozonolysis yields only ethanal. The ozonolysis of isomer of this alkene yields :



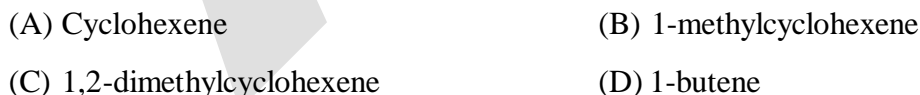
10. Which of the following elimination reactions will occur to give but-1-ene as the major product?



The above compound undergoes elimination on heating can yield which of the following products?



12. Which of the following will give same product with HBr in presence or absence of peroxide.



13. The ionic addition of HCl to which of the following compounds will produces a compound having Cl on carbon next to terminal.



EXERCISE # III

1. Which is / are true statements/ reactions?
- (A) $\text{Al}_4\text{C}_3 + \text{H}_2\text{O} \longrightarrow \text{CH}_4$ (B) $\text{CaC}_2 + \text{H}_2\text{O} \longrightarrow \text{C}_2\text{H}_2$
- (C) $\text{Mg}_2\text{C}_3 + \text{H}_2\text{O} \longrightarrow \text{CH}_3\text{C} \equiv \text{CH}$ (D) $\text{Me}_3\text{C}-\text{H} + \text{KMnO}_4 \xrightarrow[\Delta]{\text{H}^+} \text{Me}_3\text{C}-\text{OH}$
2. Which reagent is the most useful for distinguishing compound I from the rest of the compounds
- $\text{CH}_3\text{CH}_2\text{C} \equiv \text{CH}$ $\text{CH}_3\text{C} \equiv \text{CCH}_3$ $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ $\text{CH}_3\text{CH}=\text{CH}_2$
- I II III IV
- (A) Alk. KMnO_4 (B) Br_2/CCl_4 (C) $\text{Br}_2/\text{CH}_3\text{COOH}$ (D) Ammonical AgNO_3
3. $\text{C} \xleftarrow[\text{H}_2\text{O}_2/\text{OH}^-]{\text{BH}_3/\text{THF}} \text{A} \xrightarrow[\text{H}_2\text{SO}_4]{\text{HgSO}_4} \text{B}$

B & C are identical when A is –

- (A) $\text{HC}\equiv\text{CH}$ (B) $\text{CH}_3-\text{C}\equiv\text{CH}$ (C) $\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_3$ (D) $\text{CH}_3-\text{CH}_2-\text{C}\equiv\text{CH}$
4. Match List-I with List-II and select the correct answer using the codes given below the lists:

List-I (Reaction)

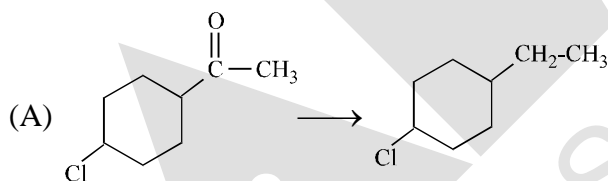
- (A) $\text{CH}_3\text{--CH=CH}_2 \rightarrow \text{CH}_3\text{--CHBr--CH}_3$
 (B) $\text{CH}_3\text{--CH=CH}_2 \rightarrow \text{CH}_3\text{--CH}_2\text{--CH}_2\text{Br}$
 (C) $\text{CH}_3\text{--CH=CH}_2 \rightarrow \text{BrCH}_2\text{--CH=CH}_2$
 (D) $\text{CH}_3\text{--CH=CH}_2 \rightarrow \text{CH}_3\text{--CHBr--CH}_2\text{Br}$

List-II (Reagents)

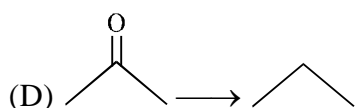
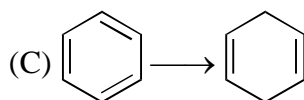
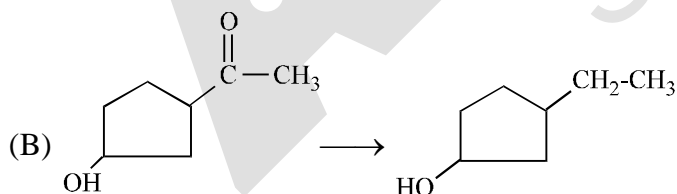
- (P) HBr
(Q) $\text{Br}_2 / \text{CCl}_4$
(R) HBr / Peroxide
(S) NBS

5. Match the column

Column I



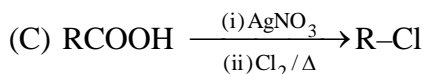
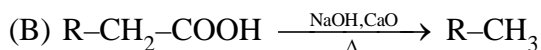
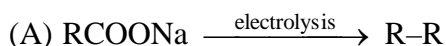
Column II



- (P) Birch reduction
- (Q) Stephen's reduction
- (R) Wolf-Kishner reduction
- (S) Clemmensen reduction

6. Match the column

Column I



Column II

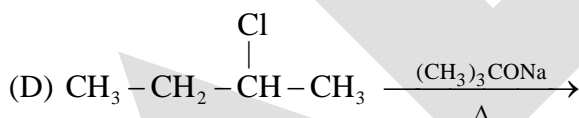
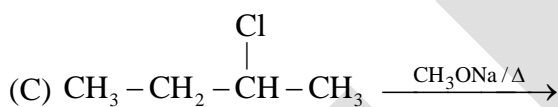
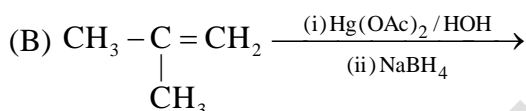
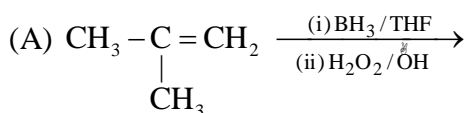
(P) Correy-House reaction

(Q) Kolbe electrolysis

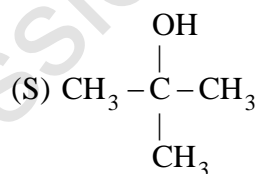
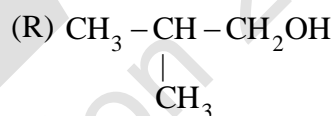
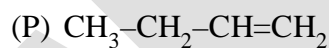
(R) Oakwood degradation / Soda lime process

(S) Hunsdiecker reaction

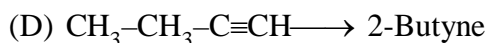
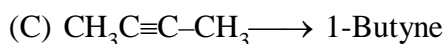
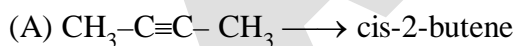
7. Column I



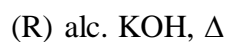
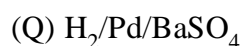
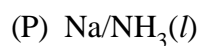
Column II



8. Column I

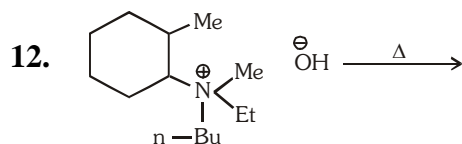


Column II



EXERCISE # (IV) (J-MAINS)

1. Which of these will not react with acetylene - [AIEEE-2002]
 (1) NaOH (2) ammonical AgNO_3 (3) Na (4) HCl
 2. What is the product formed when acetylene reacts with hypochlorous acid - [AIEEE-2002]
 (1) CH_3COCl (2) ClCH_2CHO (3) Cl_2CHCHO (4) ClCH_2COOH
 3. 1-Butene may be converted to butane by reaction with - [AIEEE-2003]
 (1) Pd/H_2 (2) $\text{Zn} - \text{HCl}$ (3) $\text{Sn} - \text{HCl}$ (4) $\text{Zn} - \text{Hg/HCl}$
 4. On mixing a certain alkane with chlorine and irradiating it with ultraviolet light, it forms only one monochloroalkane. This alkane could be - [AIEEE-2003]
 (1) neopentane (2) propane (3) pentane (4) isopentane
 5. Which one of the following is reduced with Zn-Hg/HCl to give the corresponding hydrocarbon [AIEEE-2004]
 (1) Butan-2-one (2) Acetic acid
 (3) Acetamide (4) Ethyl acetate
 6. Which one of the following has the minimum boiling point : [AIEEE-2004]
 (1) isobutane (2) 1-butyne (3) 1-butene (4) n-butane
 7. 2-Methylbutane on reacting with bromine in the presence of sunlight gives mainly [AIEEE-2005]
 (1) 2-bromo-2-methylbutane (2) 1-bromo-2-methylbutane
 (3) 1-bromo-3-methylbutane (4) 2-bromo-3-methylbutane
 8. Alkyl halides react with dialkyl copper reagent to give [AIEEE-2005]
 (1) alkyl copper halides (2) alkenes
 (3) alkenyl halides (4) alkanes
- Reaction of one molecule of HBr with one molecule of 1,3-butadiene at 40°C gives predominantly
- (1) 1-bromo-2-butene under thermodynamically controlled conditions [AIEEE-2005]
 - (2) 3-bromobutene under kinetically controlled conditions
 - (3) 1-bromo-2-butene under kinetically controlled conditions
 - (4) 3-bromobutene under thermodynamically controlled conditions
10. Acid catalyzed hydration of alkenes except ethene leads to the formation of [AIEEE-2005]
 (1) secondary or tertiary alcohol
 (2) primary alcohol
 (3) mixture of secondary and tertiary alcohols
 (4) mixture of primary and secondary alcohols
 11. Elimination of bromine from 2-bromobutane results in the formation of [AIEEE-2005]
 (1) predominantly 2-butene (2) equimolar mixture of 1 and 2-butene
 (3) predominantly 2-butyne (4) predominantly 1-butene



The alkene formed as a major product in the above elimination reaction is- [AIEEE-2006]



13. Reaction of trans-2-phenyl-1-bromocyclopentane on reaction with alcoholic KOH produces-

- (1) 4-phenyl cyclopentene (2) 2-phenyl cyclopentene [AIEEE-2006]
(3) 1-phenyl cyclopentene (4) 3-phenyl cyclopentene

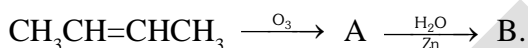
14. Phenyl magnesium bromide reacts with methanol to give- [AIEEE-2006]

- (1) A mixture of anisole and $\text{Mg}(\text{OH})\text{Br}$ (2) A mixture of benzene and $\text{Mg}(\text{OMe})\text{Br}$
(3) A mixture of toluene and $\text{Mg}(\text{OH})\text{Br}$ (4) A mixture of phenol and $\text{Mg}(\text{Me})\text{Br}$

15. Which of the following reactions will yield, 2, 2-dibromopropane [AIEEE-2007]

- (1) $\text{CH}_3-\text{C}\equiv\text{CH} + 2\text{HBr} \longrightarrow$ (2) $\text{CH}_3\text{CH}=\text{CHBr} + \text{HBr} \longrightarrow$
(3) $\text{CH}\equiv\text{CH} + 2\text{HBr} \longrightarrow$ (4) $\text{CH}_3-\text{CH}=\text{CH}_2 + \text{HBr} \longrightarrow$

16. In the following sequence of reactions, the alkene affords the compound 'B' :- [AIEEE-2008]



The compound B is

- (1) $\text{CH}_3\text{CH}_2\text{CHO}$ (2) CH_3COCH_3 (3) $\text{CH}_3\text{CH}_2\text{COCH}_3$ (4) CH_3CHO

17. The hydrocarbon which can react with sodium in liquid ammonia is [AIEEE-2008]

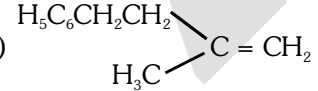
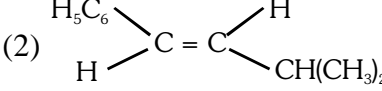
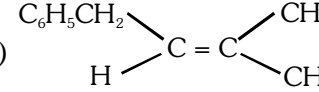
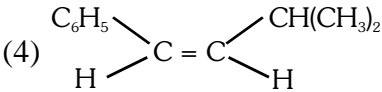
- (1) $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CCH}_2\text{CH}_2\text{CH}_3$ (2) $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$
(3) $\text{CH}_3\text{CH}=\text{CHCH}_3$ (4) $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CCH}_2\text{CH}_3$

18. The treatment of CH_3MgX with $\text{CH}_3\text{C}\equiv\text{C}-\text{H}$ produces [AIEEE-2008]

- (1) $\text{CH}_3-\text{CH}=\text{CH}_2$ (2) $\text{CH}_3\text{C}\equiv\text{C}-\text{CH}_3$ (3)  (4) CH_4

19. The main product of the following reaction is [AIEEE-2010]



- (1)  (2) 
(3)  (4) 

20. One mole of a symmetrical alkene on ozonolysis gives two moles of an aldehyde having a molecular mass of 44 u. The alkene is :- [AIEEE-2010]

- (1) Ethene (2) Propene (3) 1-Butene (4) 2-Butene

21. Ozonolysis of an organic compound gives formaldehyde as one of the products. This confirms the presence of :- [AIEEE-2011]

- (1) an isopropyl group (2) an acetylenic triple bond
(3) two ethylenic double bonds (4) a vinyl group

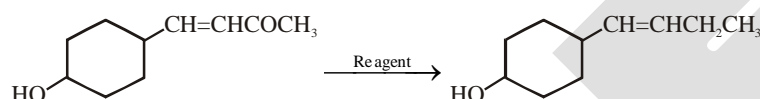
22. Ozonolysis of an organic compound 'A' produces acetone and propionaldehyde in equimolar mixture. Identify 'A' from the following compounds :- [AIEEE-2011]

- (1) 2-Methyl-1-pentene (2) 1-Pentene
(3) 2-Pentene (4) 2-Methyl-2-pentene

23. 2-Hexyne gives trans-2-Hexene on treatment with :- [AIEEE-2012]

- (1) LiAlH_4 (2) Pt/H_2 (3) Li/NH_3 (4) Pd/BaSO_4

24. In the given transformation, which of the following is the most appropriate reagent ? [AIEEE-2012]



- (1) NaBH_4 (2) $\text{NH}_2\text{NH}_2 \cdot \text{OH}^-$ (3) $\text{Zn} - \text{Hg} / \text{HCl}$ (4) $\text{Na}, \text{Liq. NH}_3$

25. The major organic compound formed by the reaction of 1, 1, 1-trichloroethane with silver powder is :- (JEE MAIN OFFLINE 2013)

- (1) 2-Butyne (2) 2-Butene (3) Acetylene (4) Ethene

26. The number and type of bonds in C_2^{2-} ion in CaC_2 are: (JEE MAIN ONLINE 2014)

- (1) Two σ bonds and one π - bond (2) Two σ bonds and two π - bonds
(3) One σ bond and two π - bonds (4) One σ bond and one π - bond

27. In the hydroboration - oxidation reaction of propene with diborane, H_2O_2 and NaOH , the organic compound formed is : (JEE MAIN ONLINE 2014)

- (1) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ (2) $(\text{CH}_3)_3\text{COH}$ (3) $\text{CH}_3\text{CHOHCH}_3$ (4) $\text{CH}_3\text{CH}_2\text{OH}$

28. Which one of the following class of compounds is obtained by polymerization of acetylene ?

(JEE MAIN ONLINE 2014)

- (1) Poly-ene (2) Poly-yne (3) Poly-amide (4) Poly-ester

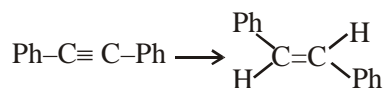
29. The gas liberated by the electrolysis of Dipotassium succinate solution is :

(JEE MAIN ONLINE 2014)

- (1) Ethyne (2) Ethene (3) Propene (4) Ethane

30. The reagent needed for converting

(JEE MAIN ONLINE 2014)




is :

(1) $\text{H}_2/\text{Lindlar Cat.}$

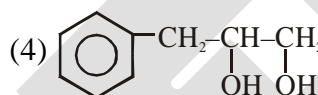
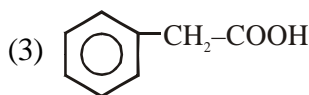
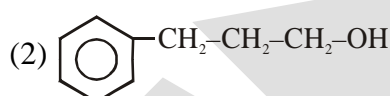
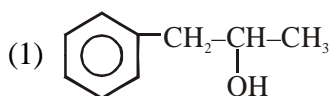
(2) Cat. Hydrogenation

(3) LiAlH_4

(4) Li/NH_3

31.  $\text{CH}_2-\text{CH}=\text{CH}_2$ on mercuration- demercuration produces the major product :-

(Jee Main online 2014)



32. The major product obtained in the photo catalysed bromination of 2-methylbutane is :-

(Jee Main online 2014)

(1) 2-bromo-2-methylbutane

(2) 2-bromo-3-methylbutane

(3) 1-bromo-2-methylbutane

(4) 1-bromo-3-methylbutane

33. In the presence of peroxide, HCl and HI do not give anti-Markownikoff's addition to alkenes because

(Jee Main online 2014)

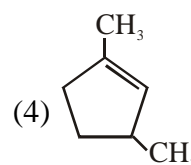
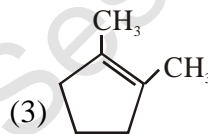
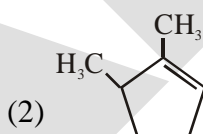
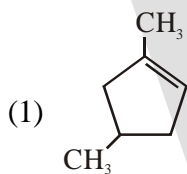
(1) All the steps are exothermic in HCl and HI

(2) One of the steps is endothermic in HCl and HI

(3) HCl is oxidizing and the HI is reducing

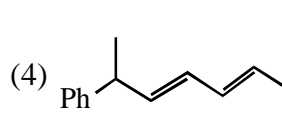
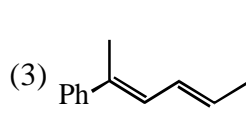
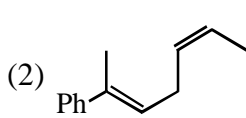
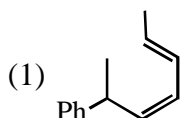
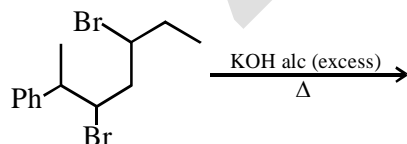
(4) Both HCl and HI are strong acids

34. Which compound would give 5-keto-2-methyl hexanal upon ozonolysis? (Jee Main offline 2015)

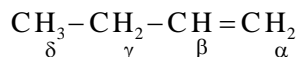


35. The major product of the following reaction is

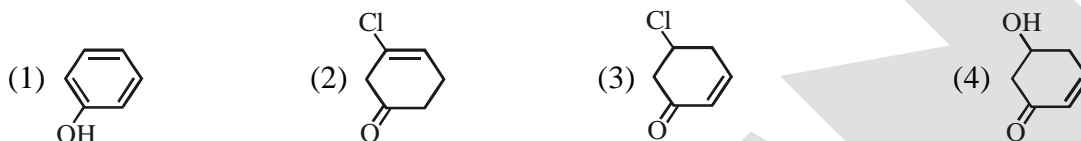
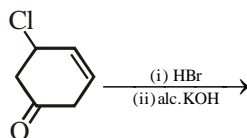
(Jee Main (Jan) 2019)



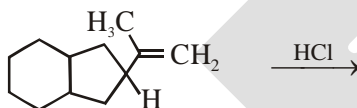
36. Which hydrogen in compound (E) is easily replaceable during bromination reaction in presence of light :
(Jee Main (Jan) 2019)



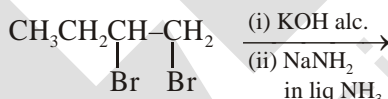
- (1) β - hydrogen (2) γ - hydrogen (3) δ - hydrogen (4) α - hydrogen
37. The major product of the following reaction is: (Jee Main (Jan) 2019)



38. The major product of the following reaction is: (Jee Main (Jan) 2019)



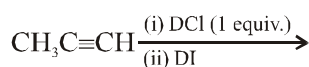
39. The major product of the following reaction is: (Jee Main (Jan) 2019)



- (1) $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$ (2) $\text{CH}_3\text{CH}_2\underset{\text{NH}_2\text{NH}_2}{\text{CH}} - \text{CH}_2$
(3) $\text{CH}_3\text{CH}=\text{C}=\text{CH}_2$ (4) $\text{CH}_3\text{CH}=\text{CHCH}_2\text{NH}_2$
40. Which one of the following alkenes when treated with HCl yields majorly an anti Markovnikov product? (Jee Main (April) 2019)

- (1) $\text{F}_3\text{C} - \text{CH} = \text{CH}_2$ (2) $\text{Cl} - \text{CH} = \text{CH}_2$
(3) $\text{CH}_3\text{O} - \text{CH} = \text{CH}_2$ (4) $\text{H}_2\text{N} - \text{CH} = \text{CH}_2$

41. The major product of the following reaction is : (Jee Main (April) 2019)



- (1) $\text{CH}_3\text{CD}(\text{Cl})\text{CHD}(\text{I})$ (2) $\text{CH}_3\text{CD}_2\text{CH}(\text{Cl})(\text{I})$
(3) $\text{CH}_3\text{CD}(\text{I})\text{CHD}(\text{Cl})$ (4) $\text{CH}_3\text{C}(\text{I})(\text{Cl})\text{CHD}_2$

42. The major product of the following addition reaction is :

(Jee Main (April) 2019)



- (1) $\text{CH}_3-\underset{\text{Cl}}{\text{CH}}-\underset{\text{OH}}{\text{CH}_2}$ (2) $\text{H}_3\text{C}-\underset{\text{OH}}{\text{CH}}-\underset{\text{Cl}}{\text{CH}_2}$ (3) $\text{H}_3\text{C}-\text{Cyclopropane}$ (4) $\text{H}_3\text{C}-\overset{\text{O}}{\parallel}-\text{CH}_3$

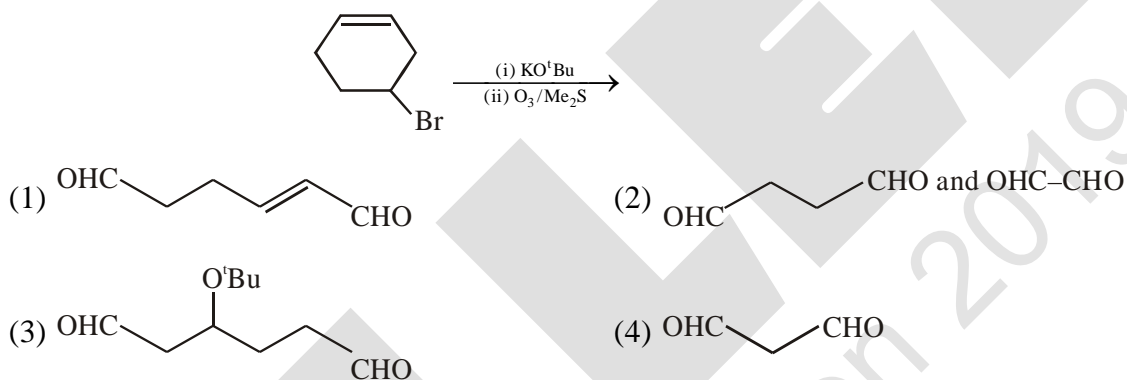
43. But-2-ene on reaction with alkaline KMnO_4 at elevated temperature followed by acidification will give :

(Jee Main (April) 2019)

- (1) one molecule of CH_3CHO and one molecule of CH_3COOH
 (2) $\text{CH}_3-\underset{\text{OH}}{\text{CH}}-\underset{\text{OH}}{\text{CH}}-\text{CH}_3$
 (3) 2 molecules of CH_3COOH
 (4) 2 molecules of CH_3CHO

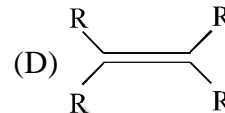
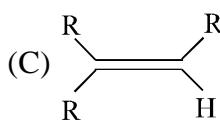
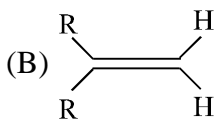
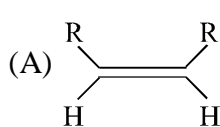
44. The major product(s) obtained in the following reaction is/are :

(Jee Main (April) 2019)

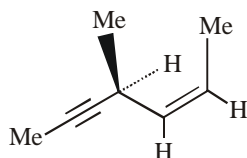



EXERCISE # IV (A) (JEE ADVANCE)

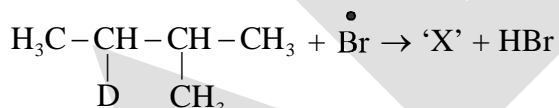
1. Propyne and propene can be distinguished by – **[IIT '2000]**
 (A) conc. H_2SO_4 (B) Br_2 in CCl_4 (C) dil. KMnO_4 (D) AgNO_3 in ammonia
2. Which one of the following alkenes will react fastest with H_2 under catalytic hydrogenation condition



3. In the presence of peroxide, hydrogen chloride and hydrogen iodide do not give anti-Markovnikov addition to alkene because – [IIT S'2001]
- (A) both are highly ionic (B) one is oxidising and the other is reducing
- (C) one of the step is endothermic in both the cases (D) All the steps are exothermic in both cases
4. The reaction of propene with HOCl proceeds via the addition of – [IIT '2001]
- (A) H^+ in first step (B) Cl^+ in first step
- (C) OH^- in first step (D) Cl^+ and OH^- in single step



5. 
- Hydrogenation of the above compound in the presence of poisoned palladium catalyst gives – [IIT '2001]
- (A) An optically active compound (B) An optically inactive compound
(C) A racemic mixture (D) A diastereomeric mixture
6. Consider the following reactions – [IIT '2002]



Identify the structure of the major product 'X'

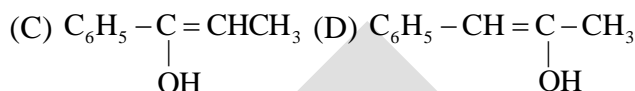
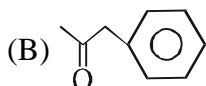
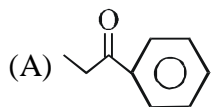
- (A) $\text{H}_3\text{C}-\underset{\text{D}}{\text{CH}}-\underset{\text{CH}_3}{\text{CH}}-\dot{\text{C}}\text{H}_2$
- (B) $\text{H}_3\text{C}-\underset{\text{D}}{\text{CH}}-\underset{\text{CH}_3}{\text{C}}-\text{CH}_3$
- (C) $\text{H}_3\text{C}-\underset{\text{D}}{\dot{\text{C}}}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3$
- (D) $\text{H}_3\text{C}-\dot{\text{C}}\text{H}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3$

7. The nodal plane in the π -bond of ethene is located in – [IIT '2002]
- (A) The molecular plane
- (B) A plane parallel to the molecular plane
- (C) A plane perpendicular to the molecular plane which contains the carbon-carbon σ -bond at right angle
- (D) A plane perpendicular to the molecular plane which contains the carbon-carbon σ -bond

8. Identify a reagent from the following list which can easily distinguish between 1-butyne and 2-butyne- [IIT '2002]

(A) Bromine, CCl_4 (B) H_2 , Lindlar catalyst
(C) Dilute H_2SO_4 , HgSO_4 (D) Ammonical Cu_2Cl_2 solution

9. $\text{C}_6\text{H}_5-\text{C}\equiv\text{C}-\text{CH}_3 \xrightarrow[\text{H}_2\text{SO}_4]{\text{HgSO}_4} \text{A}$ [IIT '2003]



10. [IIT '2003]

Number of compounds in X will be:

- (A) 2 (B) 3 (C) 4 (D) 5 [IIT '2004]

11. 2-hexyne can be converted into trans-2-hexene by the action of: [IIT '2004]

(A) $\text{H}_2-\text{Pd}-\text{BaSO}_4$ (B) Li in li NH_3 (C) H_2-PtO_2 (D) NaBH_4

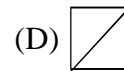
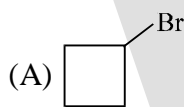
12. Cyclohexene is best prepared from cyclohexanol by which of the following: [IIT '2004]

(A) conc. H_3PO_4 (B) conc. HCl/ZnCl_2 (C) conc. HCl (D) conc. HBr

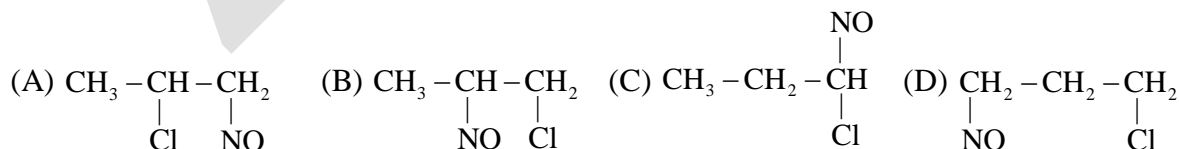
13. When Phenyl Magnesium Bromide reacts with tert. butanol, which of the following is formed? [IIT '2005]

(A) Tert. butyl methyl ether (B) Benzene
(C) Tert. butyl benzene (D) Phenol

14. 1-Bromo-3-chlorocyclobutane when treated with two equivalents of Na, in the presence of ether which of the following will be formed? [IIT '2005]



15. $\text{CH}_3-\text{CH}=\text{CH}_2 + \text{NOCl} \rightarrow \text{P}$ [IIT 2006]
Identify the adduct.



16. The number of stereoisomers obtained by bromination of trans-2-butene is [IIT 2007]

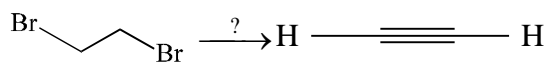
(A) 1 (B) 2 (C) 3 (D) 4

17. The number of structural isomers for C_6H_{14} is [IIT 2007]

(A) 3 (B) 4 (C) 5 (D) 6

18. The reagent(s) for the following conversion,

[IIT 2007]



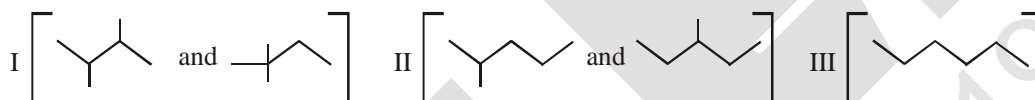
is / are

- (A) alcoholic KOH
(B) alcoholic KOH followed by NaNH_2
(C) aqueous KOH followed by NaNH_2
(D) $\text{Zn} / \text{CH}_3\text{OH}$

19. The synthesis of 3-octyne is achieved by adding a bromoalkane into a mixture of sodium amide and an alkyne. The bromoalkane and alkyne respectively are **[IIT-2010]**

- (A) $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{C} \equiv \text{CH}$
 (B) $\text{BrCH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{C} \equiv \text{CH}$
 (C) $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{C} \equiv \text{CH}$
 (D) $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{C} \equiv \text{CH}$

20. Isomers of hexane, based on their branching, can be divided into three distinct classes as shown in the figure. [IIT-2014]

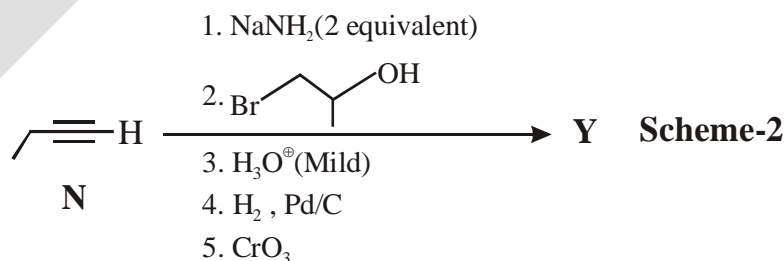
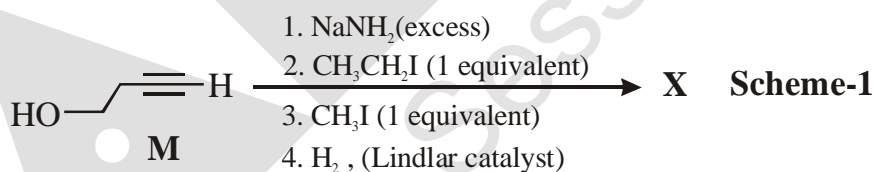


The correct order of their boiling point is

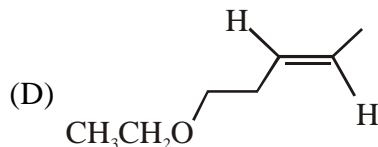
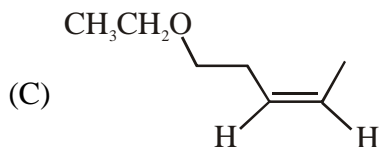
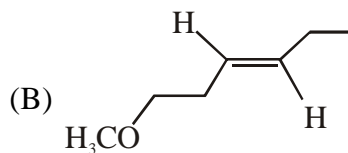
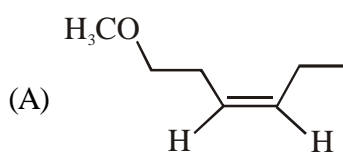
- (A) $I > II > III$ (B) $III > II > I$ (C) $II > III > I$ (D) $III > I > II$

Paragraph For Question 21 and 22

Schemes 1 and 2 describe sequential transformation of alkynes M and N. Consider only the major products formed in each step for both the schemes. [IIT-2014]



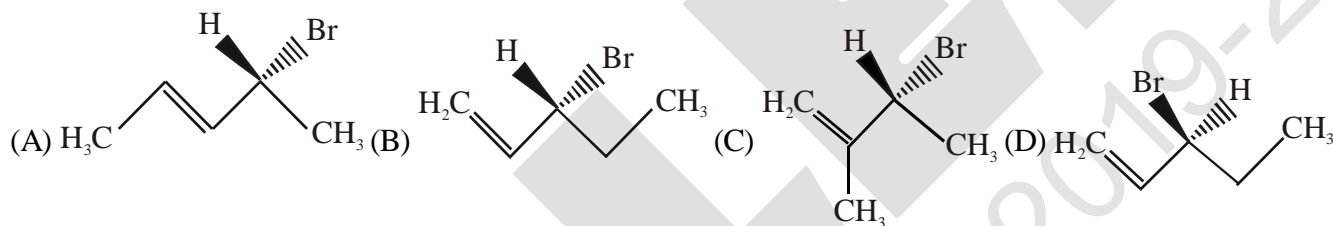
21. The product X is -



22. The correct statement with respect to product Y is -

- (A) It gives a positive Tollens test and is a functional isomer of X
 (B) It gives a positive Tollens test and is a geometrical isomer of X
 (C) It gives a positive Iodoform test and is a functional isomer of X
 (D) It gives a positive Iodoform test and is a geometrical isomer of X

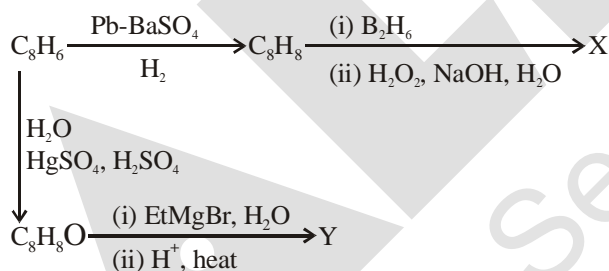
23. Compound(s) that on hydrogenation produce(s) optically inactive compound(s) is (are) [IIT-2015]



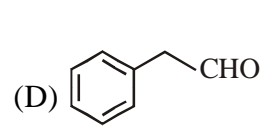
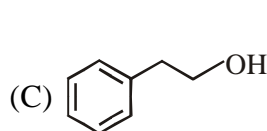
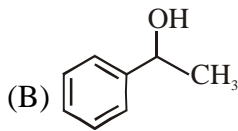
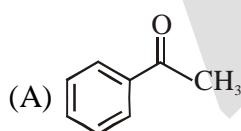
Paragraph For Questions 24 and 25

In the following reaction

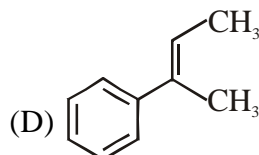
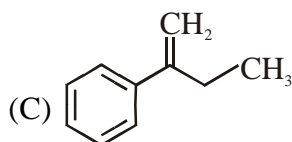
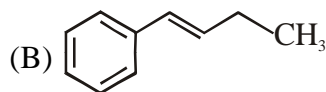
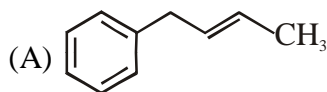
[IIT-2015]



24. Compound X is :

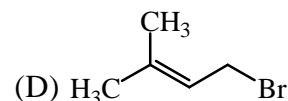
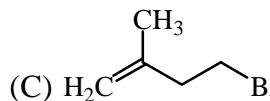
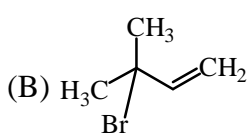
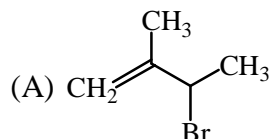
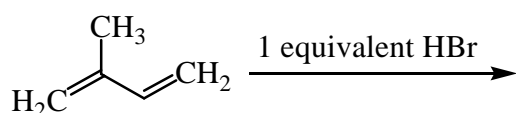


25. The major compound Y is :



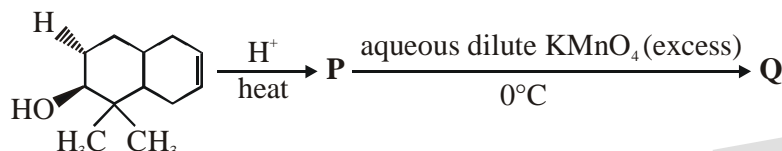
26. In the following reaction, the major product is -

[IIT-2015]



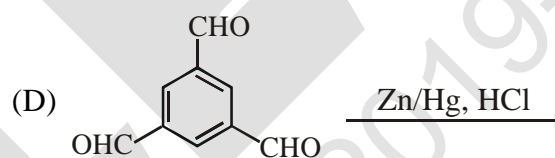
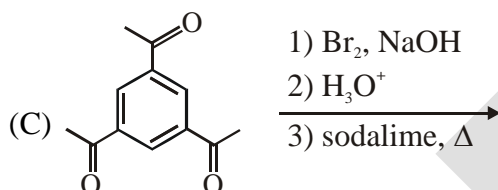
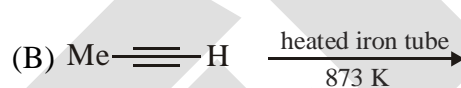
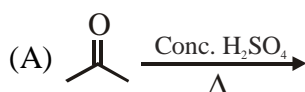
27. The number of hydroxyl group(s) in Q is

[IIT-2015]



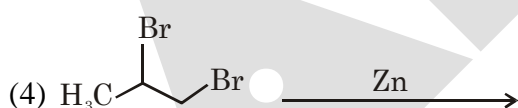
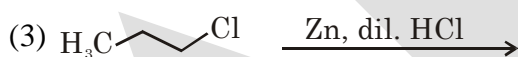
28. The reaction(s) leading to the formation of 1,3,5-trimethylbenzene is (are)

[IIT-2018]

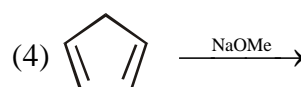
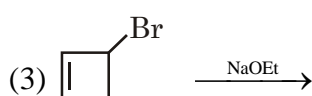
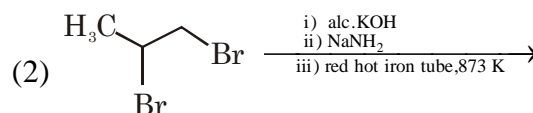
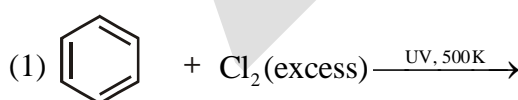


29. Which of the following reactions produce(s) propane as a major product?

[IIT-2019]



30. Choose the correct option(s) that give(s) an aromatic compound as the major product.



[IIT-2019]

ANSWER KEY

EXERCISE # I

- | | | | | |
|---------|---------|---------|---------|---------|
| 1. (A) | 2. (C) | 3. (B) | 4. (C) | 5. (D) |
| 6. (C) | 7. (C) | 8. (B) | 9. (A) | 10. (D) |
| 11. (B) | 12. (A) | 13. (C) | 14. (D) | 15. (C) |
| 16. (B) | 17. (A) | 18. (B) | 19. (A) | 20. (D) |
| 21. (C) | 22. (B) | 23. (C) | 24. (A) | 25. (C) |
| 26. (B) | 27. (A) | 28. (C) | 29. (A) | 30. (B) |
| 31. (B) | 32. (D) | | | |

EXERCISE # II

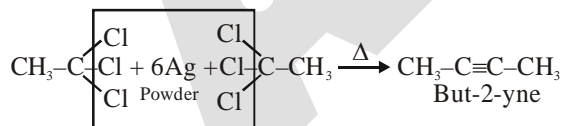
- | | | | | |
|--------------|-----------|-------------|------------|--------------|
| 1. (B) | 2. (C) | 3. (B) | 4. (B) | 5. (A,B,C,D) |
| 6. (A,B,C,D) | 7. (A,B) | 8. (A,B) | 9. (A,B,C) | 10. (B,C) |
| 11. (B,C,D) | 12. (A,C) | 13. (A,B,D) | | |

EXERCISE # III

- | | | |
|----------------------------------|------------------------------------|----------|
| 1. (A,B,C,D) | 2. (D) | 3. (A,C) |
| 4. (A)→P ; (B)→R ; (C)→S ; (D)→Q | 5. (A)→S ; (B)→R ; (C)→P ; (D)→R,S | |
| 6. (A)→Q ; (B)→R ; (C)→S ; (D)→P | 7. (A)→R ; (B)→S ; (C)→Q ; (D)→P | |
| 8. (A)→Q ; (B)→P ; (C)→S ; (D)→R | | |

EXERCISE # (IV) (J-MAINS)

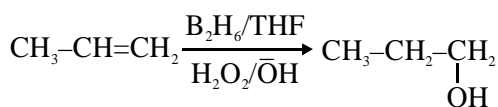
- | | | | | |
|---------|---------|---------|---------|---------|
| 1. (1) | 2. (3) | 3. (1) | 4. (1) | 5. (1) |
| 6. (1) | 7. (1) | 8. (4) | 9. (1) | 10. (1) |
| 11. (1) | 12. (2) | 13. (4) | 14. (2) | 15. (1) |
| 16. (4) | 17. (2) | 18. (4) | 19. (2) | 20. (4) |
| 21. (4) | 22. (4) | 23. (3) | 24. (2) | |
| 25. (1) | | | | |



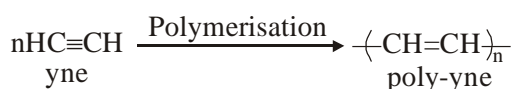
26. (3)



27. (1)



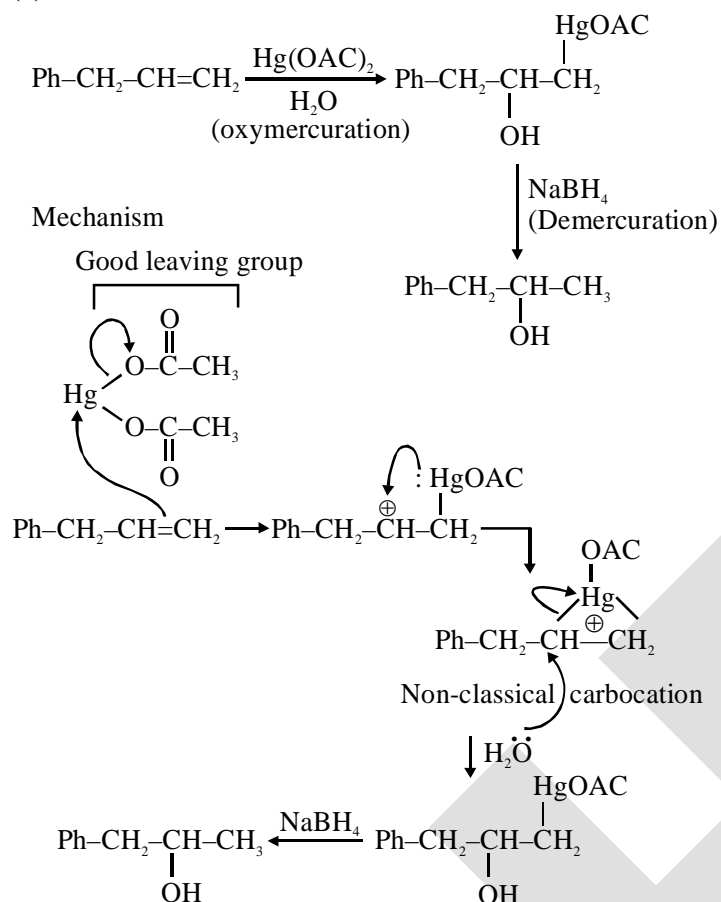
28. (2)



29. (2)

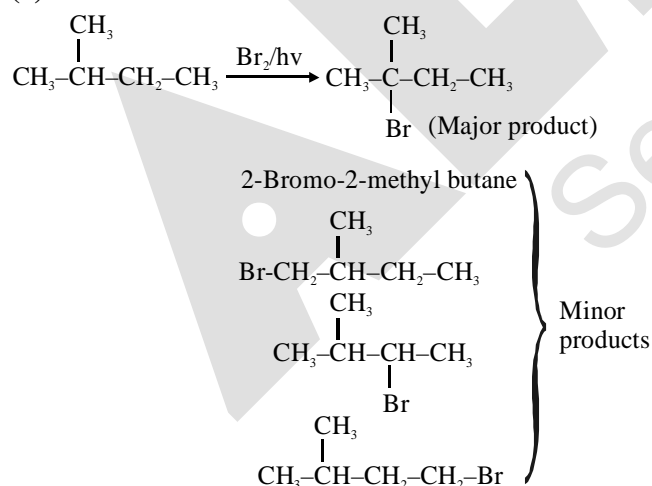
30. (4)

31. (1)



Rearrangement of carbocation formed is not possible due to formation of cyclic non-classical carbocation.

32. (1)



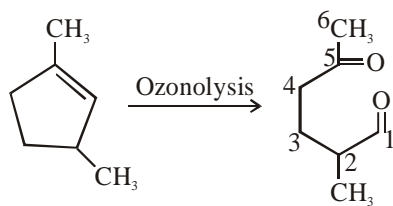
selectivity ratio for bromination is

$1^\circ : 2^\circ : 3^\circ :: 1 : 82 : 1600$

Hence 3° product will be major product.

33. (2)

34. (4)



5-Keto-2-Methylhexanal

35. Ans. (3)

36. Ans. (2)

37. Ans. (1)

38. Ans. (1)

39. Ans. (1)

40. Ans. (1)

41. Ans. (4)

42. Ans. (2)

43. Ans. (3)

44. Ans. (2)

EXERCISE # IV (A) (JEE ADVANCE)

1. (D)

2. (A)

3. (C)

4. (B)

5. (B)

6. (B)

7. (A)

8. (D)

9. (A)

10. (B)

11. (B)

12. (A)

13. (B)

14. (D)

15. (A)

16. (A)

17. (C)

18. (B)

19. (D)

20. (B)

21. (A)

22. (C)

23. (B,D)

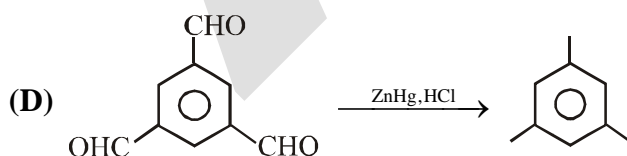
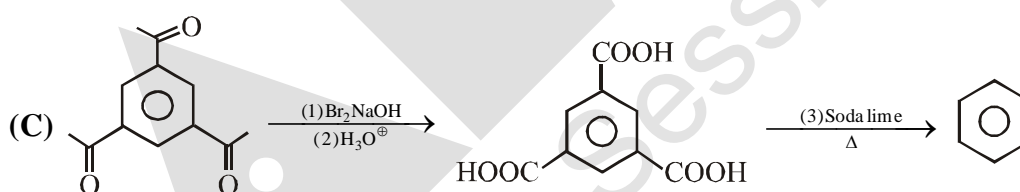
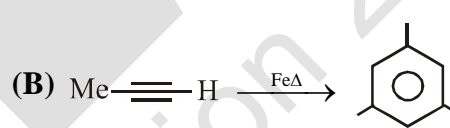
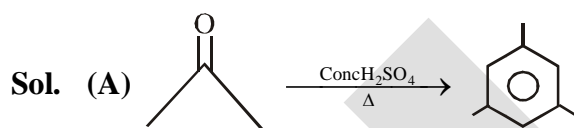
24. (C)

25. (D)

26. (D)

27. (4)

28. (A,B,D)



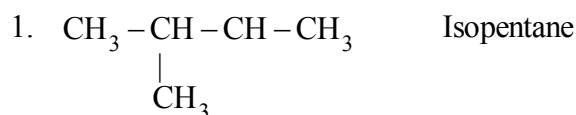
29. Ans. (2,3)

30. Ans. (2,4)

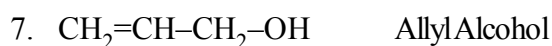
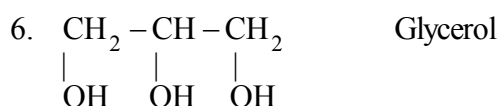
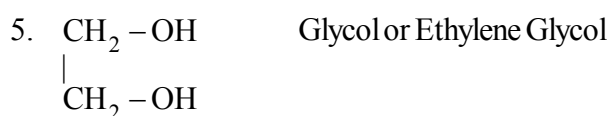
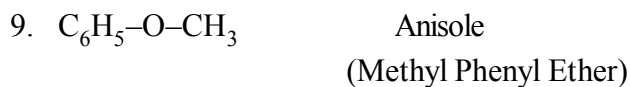
Important Notes

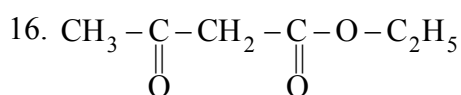
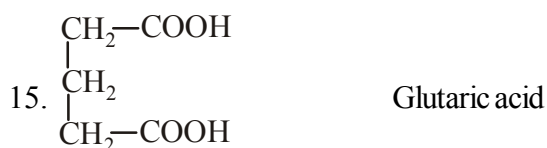
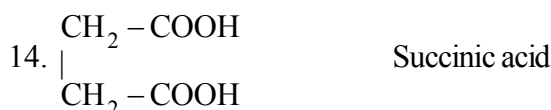
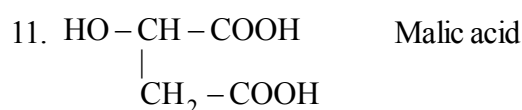
NURTURE COURSE

**NOMENCLATURE OF ORGANIC COMPOUND
AND COMMON NAMES**

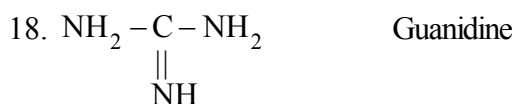
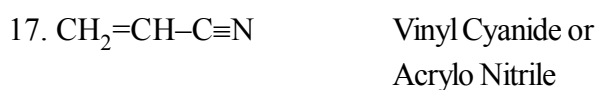
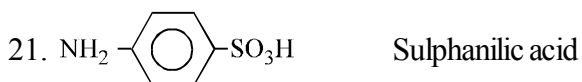
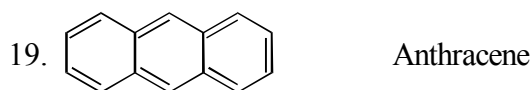
NOMENCLATURE OF ORGANIC COMPOUND AND COMMON NAMES
-ESSENTIAL COMMON NAMES-
ALKANE

ALKENE

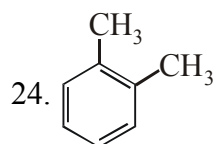
ALKYL HALIDE

ALCOHOL

ETHER

KETONE

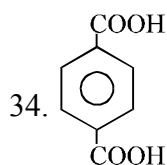
CARBOXYLIC ACID


Aceto Acetic Ester (AAE)
or Ethyl Aceto Acetate

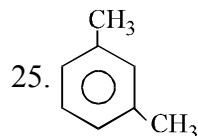
N-DERIVATIVES

AROMATIC COMPOUNDS




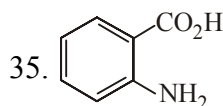
o-xylene



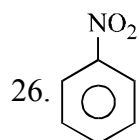
Terephthalic acid



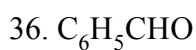
m-xylene



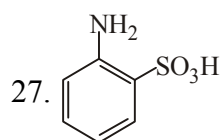
Anthranilic acid (o-aminobenzoic acid)



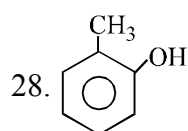
Nitrobenzene (oil of mirbane)



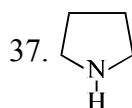
Benzaldehyde



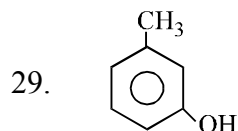
Ortho-aniline

HETEROCYCLIC COMPOUNDS

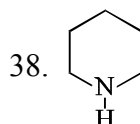
o-Cresol



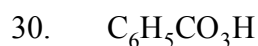
Pyrrolidine



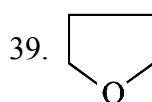
m-Cresol



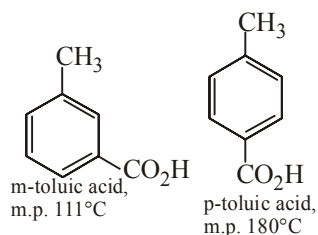
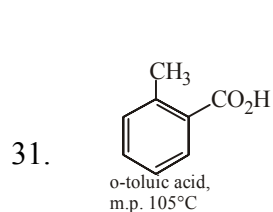
Piperidine



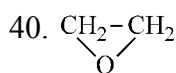
Perbenzoic acid



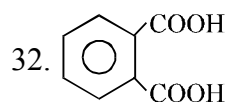
Tetrahydrofuran (THF)



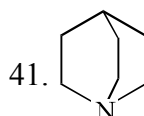
Toluic acids



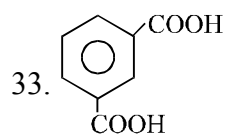
Oxirane or Ethylene Oxide or



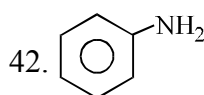
Phthalic acid



Quinuclidine



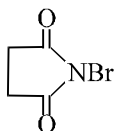
Isophthalic acid



Aniline

SOME REAGENTS

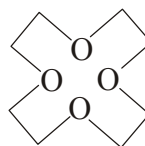
43. Grignard's reagent RMgX
44. NBS $\text{N-Bromosuccinimide}$


POLAR PROTIC SOLVENTS

45. $\text{H}-\text{O}-\text{H}$ Water
46. $\text{R}-\text{O}-\text{H}$ Alcohol
47. Phenol
48. $\text{CH}_3-\text{C}(=\text{O})-\text{OH}$ Acetic acid
49. HF Hydrogen Fluoride
50. NH_3 Ammonia

POLAR APROTIC SOLVENTS

51. DMS Dimethyl sulphide $\text{CH}_3-\text{S}-\text{CH}_3$
52. DMSO Dimethyl sulphoxide $\text{Me}_2\text{S}=\text{O}$
53. HMPT Hexamethylphosphoramide
or
HMPTA $\text{O}=\text{P}-(\text{NMe}_2)_3$
54. DMF Dimethyl formamide
 $\text{H}-\text{C}(=\text{O})-\text{NMe}_2$
55. Crown ethers Cyclic polyethers



(12 - C - 4)

-DESIRABLE COMMON NAMES-**ALKANES**

1. $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 - \text{C} - \text{CH} - \text{CH}_3 \\ | \quad | \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$ Triptane
2. $\begin{array}{c} -\text{CH}_2 - \text{CH}_2 - \text{CH} - \text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$ Isopentyl Group

ALKENES

3. $\text{CH}_3 - \text{CH}_2 - \text{CH} = \text{CH}_2$ α -Butylene
4. $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3$ β -Butylene
5. $\begin{array}{c} \text{CH}_3 - \text{C} = \text{CH}_2 \\ | \\ \text{CH}_3 \end{array}$ Iso Butylene

ALKYNES

6. $\text{HC} \equiv \text{CH}$ Purified Acetylene or Norcelyne
7. $\text{CH}_3 - \text{C} \equiv \text{CH}$ Allylene

ETHER

8. $\text{CH}_3\text{CH}(\text{OCH}_3)_2$ Methylal

ALDEHYDE

9. $\begin{array}{c} \text{CHO} \\ | \\ \text{COOH} \end{array}$ Glyoxalic acid
10. $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 - \text{C} - \text{CHO} \\ | \\ \text{CH}_3 \\ \text{or} \\ (\text{CH}_3)_3\text{C} - \text{CHO} \end{array}$ Pivaldehyde
11. $(\text{CH}_3)_2\text{CHCHO}$ Isobutyraldehyde
12. $\begin{array}{c} \text{CH}_3 - \text{C} - \text{C} - \text{CH}_3 \\ || \quad || \\ \text{O} \quad \text{O} \end{array}$ Dimethyl Glyoxal

13. $\begin{array}{c} \text{CH}_3 - \text{C} - \text{C} - \text{H} \\ || \quad || \\ \text{O} \quad \text{O} \end{array}$ Methyl Glyoxal or Pyruvialdehyde

KETONE

14. $\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{C} = \text{CH} - \text{C} - \text{CH} = \text{C} \diagdown \\ \diagdown \quad || \quad \diagup \\ \text{CH}_3 \quad \text{O} \quad \text{CH}_3 \end{array}$ Phorone
15. $\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{C} = \text{CH} - \text{C} - \text{CH}_3 \\ \diagdown \quad || \\ \text{CH}_3 \quad \text{O} \end{array}$ Mesityl Oxide
16. $\text{H}_2\text{C} = \text{C} = \text{O}$ Ketene

CARBOXYLIC ACID

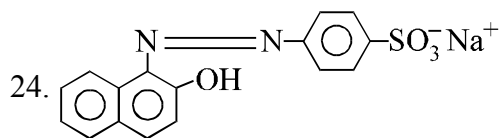
17. $\text{CH}_3 - \text{CO} - \text{COOH}$ Pyruvic Acid
18. $\begin{array}{c} \text{C}_6\text{H}_5 - \text{CH} - \text{COOH} \\ | \\ \text{OH} \end{array}$ Mandelic Acid
19. NH_2COOH Carbamic Acid (Amino formic Acid)

20. $\begin{array}{c} \text{COOH} \\ | \\ \text{COOH} \end{array}$ Oxalic acid

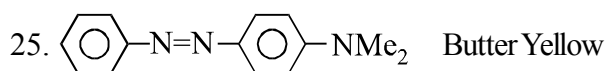
ACID DERIVATIVES

21. $\begin{array}{c} \text{Cl} - \text{C} - \text{C} - \text{Cl} \\ || \quad || \\ \text{O} \quad \text{O} \end{array}$ Oxalyl Chloride
22. $\text{NH}_2\text{COONH}_4$ Ammonium Carbamate
23. $\begin{array}{c} \text{NH}_2 - \text{C} - \text{C} - \text{NH}_2 \\ || \quad || \\ \text{O} \quad \text{O} \end{array}$ Oxanamide

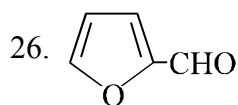
AROMATIC COMPOUNDS



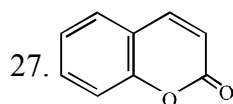
Orange II



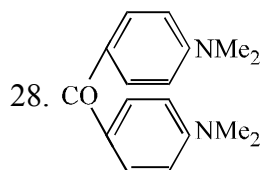
Butter Yellow



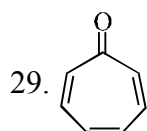
Furfural



Coumarine

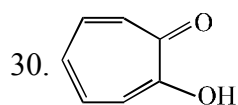


Michler's Ketone



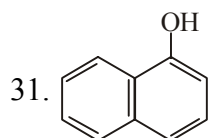
Tropone

(Cycloheptatrienone)

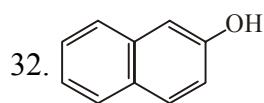


Tropolone

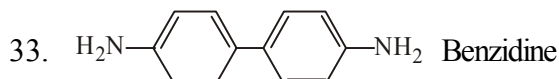
(Cycloheptatrienolone)



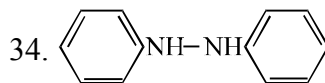
α -naphthol



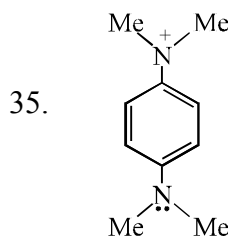
β -naphthol



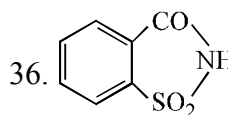
Benzidine



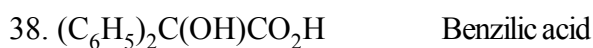
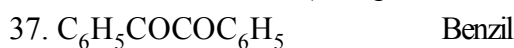
Hydrazobenzene



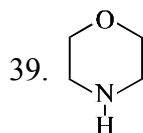
Wurster salts



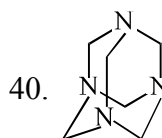
Saccharin (o-sulphobenzoic imide)



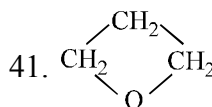
HETEROCYCLIC COMPOUNDS



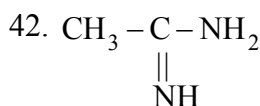
Morpholine



Hexa-methylenetetramine or Urotropine

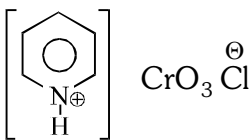
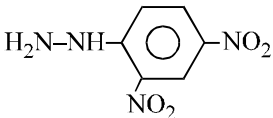


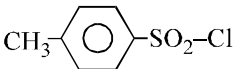
Oxitane



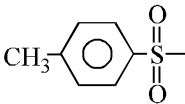
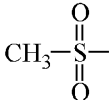
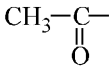
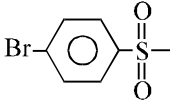
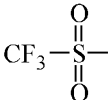
Amidine

SOME REAGENTS

43. LAH	Lithium aluminium hydride : LiAlH_4
44. SBH	Sodium borohydride NaBH_4
45. PCC	Pyridinium chlorochromate 
46. Raney Nickel	Ni-Al alloy
47. Wilkinson's	Tris(Triphenylphosphine) catalyst chlororhodium (I) $(\text{PPh}_3)_3\text{RH}^+\text{Cl}^-$
48. Bayer's reagent	1% dil. alkaline aq. sol. of KMnO_4
49. Braddy's reagent 2,4 DNP	
50. Liemieux reagent	$\text{NaIO}_4 + \text{dil. alk. KMnO}_4$

51. TEL	Tetra ethyl lead
52. Gillman's reagent	$\text{R}_2\text{CuLi}/[\text{R}_2\text{Cu}]^-\text{Li}^+$
53. Tollen's reagent	alk. sol. of AgNO_3
54. Fehling's reagent	alk. sol. of CuSO_4
55. Hinsberg's reagent	

SOME GROUPS

56. Ts	Tosyl	
57. Ms	Mesyl	
58. Ac	Acyl	
59. Bs	Brosyl	
60. Tf	Triflate	

EXERCISE # I

Q.1 How many 1° carbon atom will be present in a simplest open chain hydrocarbon having two 3° and one 2° carbon atom ?

- (A) 3 (B) 4 (C) 5 (D) 6

Q.2 Alicyclic compounds are :

- (A) Aromatic compounds (B) Aliphatic cyclic compounds
(C) Heterocyclic compounds (D) None of the above

Q.3 How many 1° , 2° , 3° C atoms does 1, 3, 5-Trimethyl cyclohexane have?

- (A) 3, 6, 0 (B) 3, 4, 2 (C) 0, 3, 6 (D) 3, 3, 3

Q.4 The compound which has one isopropyl group is:

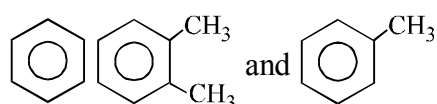
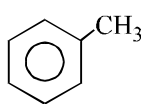
- (A) 2,2,3,3-Tetramethyl pentane (B) 2,2-Dimethyl pentane
(C) 2,2,3-Trimethyl pentane (D) 2-Methyl pentane

Q.5 Which of the following is the first member of ester homologous series?

- (A) Ethyl ethanoate (B) Methyl ethanoate
(C) Methyl methanoate (D) Ethyl methanoate

Q.6 A group closely related compounds which can be expressed by a general formula & in which two consecutive members differ by 14 in their molecular masses is called

- (A) a heterogeneous series (B) a homologous series
(C) a homogeneous series (D) a electrochemical series

Q.7  and 

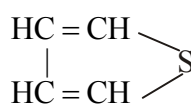
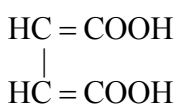
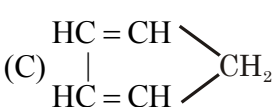
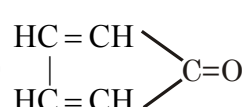
Number of secondary carbon atoms present in the above compounds are respectively:

- (A) 6,4,5 (B) 4,5,6 (C) 5,4,6 (D) 6,2,1

Q.8 The molecular formula of the first member of the family of alkenynes and its name is given by the set

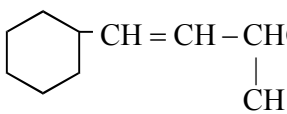
- (A) C_3H_6 , Alkene (B) C_5H_6 , Pent-1-en-3-yne
(C) C_6H_8 , Hex-1-en-5-yne (D) C_4H_4 , Butenyne

Q.9 Which of the following is a heterocyclic compound :

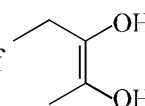
- (A)  (B)  (C)  (D) 

Q.10 The correct IUPAC name of the compound $\text{CH}_3 - \text{CH}_2 - \overset{\text{CH}_3}{\underset{\text{C}_2\text{H}_5}{\text{C}}} = \text{C} - \text{CH} - \overset{\text{CH}_3}{\text{C}} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$:

- (A) 5-Ethyl-3, 6-dimethyl non-3-ene (B) 5-Ethyl-4, 7-dimethyl non-3-ene
(C) 4-Methyl-5, 7-diethyl oct-2-ene (D) 2,4-Ethyl-5-methyl oct-2-ene

Q.11 The IUPAC name of  is:

- (A) 1-Cyclohexyl-3-methyl pent-1-ene (B) 3-Methyl-5-cyclohexyl pent-1-ene
(C) 1-Cyclohexyl-3-ethyl but-1-ene (D) 1-Cyclohexyl-3,4-dimethyl but-1-ene

Q.12 IUPAC name of  is:

- (A) But-2-ene-2,3-diol (B) Pent-2-ene-2,3-diol
(C) 2-Methylbut-2-ene-2,3-diol (D) Pent-3-ene-3,4-diol

Q.13 IUPAC name of $\text{CH}_2=\text{CH}-\text{CN}$ is:

- (A) Ethenenitrile (B) Vinyl cyanide (C) Cyano ethene (D) Prop-2-enenitrile

Q.14 The IUPAC name of $\text{CH}_3\text{CH}_2-\underset{\text{CH}_3}{\text{N}}-\text{CH}_2\text{CH}_3$ is:

- (A) N-Methyl-N-ethyl ethanamine (B) Diethyl methanamine
(C) N-Ethyl-N-methyl ethanamine (D) Methyl diethyl ethanamine

Q.15 The IUPAC name of acetyl acetone is :

- (A) Pentane-2,5- dione (B) Pentane -2,4-dione
(C) Hexane-2,4-dione (D) Butane-2,4-dione

Q.16 When vinyl & allyl are joined each other, we get

- (A) Conjugated alkadiene (B) cumulative alkadiene
(C) Isolated alkadiene (D) Allenes

Q.17 (a)  and (b) 

True statement for the above compounds is :

- (A) (a) is phenol while (b) is alcohol (B) Both (a) and (b) are primary alcohol
(C) (a) is primary and (b) is secondary alcohol (D) (a) is secondary and (b) is primary alcohol

Q.18 The IUPAC name of the following structure $(\text{CH}_3)\text{C}.\text{C}.\text{C}.\text{C}(\text{CH}_3)\text{CH}(\text{CH}_3)$ is:

- (A) 3-Methylhex-4-yn-2-ene (B) 3-Methylhex-2-en-4-yne
(C) 4-Methylhex-4-en-4-yne (D) All are correct

Q.19 The IUPAC name of the following structure is $[\text{CH}_3\text{CH}(\text{CH}_3)]_2 \text{C}(\text{CH}_2\text{CH}_3)\text{C}(\text{CH}_3) \text{C}(\text{CH}_2\text{CH}_3)_2$

- (A) 3,5-Diethyl-4,6-dimethyl-5-[1-methylethyl]hept-3-ene
(B) 3,5-Diethyl-5-isopropyl-4,6-dimethylhept-2-ene
(C) 3,5-Diethyl-5-propyl-4,6-dimethylhept-3-ene
(D) None of these

Q.20 The correct IUPAC name of $\text{CH}_3 - \text{CH}_2 - \underset{\text{CH}_2}{\overset{\text{||}}{\text{C}}} - \text{COOH}$ is:

- (A) 2-Methyl butanoic acid (B) 2-Ethylprop-2-enoic acid
(C) 2-Carboxybutene (D) None of the above

Q.21 The correct IUPAC name of 2-ethylpent-3-yne is:

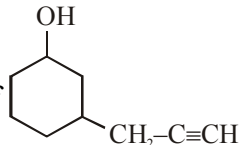
- (A) 3-Methyl hex-4-yne (B) 4-Ethyl pent-2-yne
(C) 4-methyl hex-2 yne (D) None of these

Q.22 All the following IUPAC names are correct except:

- (A) 1-Chloro-1-ethoxy propane (B) 1-Amino-1-ethoxypropane
(C) 1-Ethoxy-2-propanol (D) 1-Ethoxy-1-propanamine

Q.23 The IUPAC name of the compound $\text{CH}_3\text{CH} = \text{CHCH} = \text{CHC} \equiv \text{CCH}_3$ is:

- (A) Octa-4,6-diene-2-yne (B) Octa-2,4-diene-6-yne
(C) Oct-2-yne-4,6-diene (D) Oct-6-yne-2,4-diene

Q.24 The correct IUPAC name of 

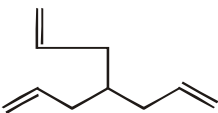
- (A) 3-Cyclohexanol Propyne (B) 3-[3-Hydroxy Cyclohexyl] Propyne
(C) 3-Propynyl Cyclohexanol (D) 3-(2-propynyl) Cyclohexanol

Q.25 The IUPAC name of β -ethoxy- α -hydroxy propionic acid (trivial name) is:

- (A) 1,2-Dihydroxy-1-oxo-3-ethoxy propane (B) 1-Carboxy-2-ethoxy ethanol
(C) 3-Ethoxy-2-hydroxy propanoic acid (D) All above

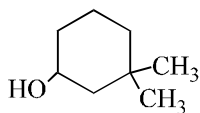
Q.26 As per IUPAC rules, which one of the following groups, will be regarded as the principal functional group ?

- (A) $-\text{C} \equiv \text{C}-$ (B) $-\text{OH}$ (C) $-\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-$ (D) $-\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-\text{H}$

Q.27 The IUPAC name of the compound  is :

- (A) 4-Prop-1-enyl hepta-1,6-diene (B) 4-Propylidene hepta-1,6-diene
(C) 4-Propenyl hepta-1,6-diene (D) 4-[Prop-2-enyl] hepta-1,6-diene

Q.28 The IUPAC name of the given compound is:



- (A) 1,1-Dimethyl-3-hydroxy cyclohexane (B) 3,3-Dimethyl-1-hydroxy cyclohexane
(C) 3,3-Dimethylcyclohexanol (D) 1,1-Dimethylcyclohexan-3-ol

Q.29 The IUPAC name of $(C_2H_5)_2NCH_2CH(Cl)COOH$ is:

- (A) 2-Chloro-4-N-ethylpentanoic acid (B) 2-Chloro-3-(N,N-diethyl amino)-propanoic acid
(C) 2-Chloro-2-oxo diethylamine (D) 2-Chloro-2-carboxy-N-ethyl ethane

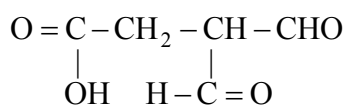
Q.30 The IUPAC name of the compound is $CH_3 - \underset{\substack{| \\ CH_3}}{CH} - \overset{\substack{| \\ Ph}}{CH} - NH_2$

- (A) 1-Amino-1-phenyl-2-methyl propane (B) 2-Methyl-1-phenyl propan-1-amine
(C) 2-Methyl-1-amino-1-phenyl propane (D) 1-Isopropyl-1-phenyl methyl amine

Q.31 Which of the following compound is wrongly named ?

- (A) $CH_3CH_2CH_2\underset{\substack{| \\ Cl}}{CH}COOH$; 2-Chloro pentanoic acid
(B) $CH_3C \equiv C\underset{\substack{| \\ CH_3}}{CH}COOH$; 2-Methyl hex-3-enoic acid
(C) $CH_3CH_2CH=CHCOCH_3$; Hex-3-en-2-one
(D) $CH_3 - \underset{\substack{| \\ CH_3}}{CH}CH_2CH_2CHO$; 4-Methyl pentanal

Q.32 The correct IUPAC name of the following compound is:



- (A) 3,3-Diformylpropanoic acid (B) 3-Formyl-4-oxo-butanoic acid
(C) 3,3-Dioxo propanoic acid (D) 3,3-Dicarbaldehyde propanoic acid

Q.33 The correct IUPAC name of compound $\text{CH}_3 - \text{CH}_2 - \text{C} - \text{CH} - \text{CHO}$ is :



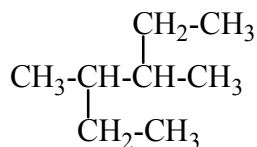
(A) 2-Cyano-3-oxopentanal

(B) 2-Formyl-3-oxopentanenitrile

(C) 2-Cyanopentane-1,3-dione

(D) 1,3-Dioxo-2-cyanopentane

Q.34 IUPAC name of compound



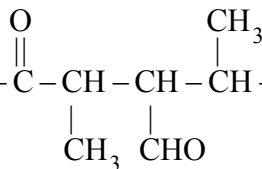
(A) 2, 3-diethyl butane

(B) 2-ethyl-3-methyl pentane

(C) 3-methyl-2-ethyl pentane

(D) 3,4-dimethyl hexane

Q.35 The IUPAC name of compound $\text{CH}_3 - \text{C} - \text{CH} - \text{CH} - \text{CH} - \text{CH}_3$ is:



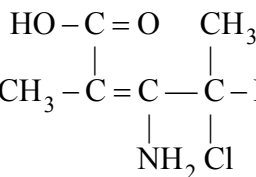
(A) 3,5-Dimethyl-4-Formyl pentanone

(B) 1-Isopropyl-2-methyl-4-oxo butanal

(C) 2-Isopropyl-3-methyl-4-oxo pentanal

(D) None of the above

Q.36 The IUPAC name of compound $\text{CH}_3 - \text{C} = \text{C} - \text{C} - \text{H}$ is :



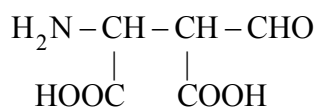
(A) 2-Amino-3-chloro-2-methylpent-2-enoic acid

(B) 3-Amino-4-chloro-2-methylpent-2-enoic acid

(C) 4-Amino-3-chloro-2-methylpent-2-enoic acid

(D) All of the above

Q.37 The IUPAC name of the structure is:



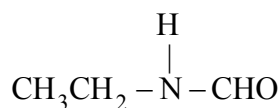
(A) 3-Amino-2-formyl butane-1, 4-dioic acid

(B) 3-Amino-2, 3-dicarboxy propanal

(C) 2-Amino-3-formyl butane-1, 4-dioic acid

(D) 1-Amino-2-formyl succinic acid

Q.38 One among the following is the correct IUPAC name of the compound



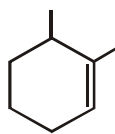
(A) N-Formyl aminoethane

(B) N-Ethyl formyl amine

(C) N-Ethyl methanamide

(D) Ethylamino methanal

Q.39 The IUPAC name of the structure is :



- (A) 1,2-Dimethyl-Cyclohexane (B) 1,6-Dimethyl-Cyclohexene
(C) 1,2-Dimethyl-Cyclohex-2-ene (D) 2,3-Dimethyl-Cyclohexane

Q.40 The IUPAC name of $\text{C}_6\text{H}_5\text{CH}=\text{CH}-\text{COOH}$ is :

- (A) Cinnamic acid (B) 1-Phenyl-2-carboxy ethane
(C) 3-Phenyl prop-2-enoic acid (D) Dihydroxy-3-phenyl propionic acid

Q.41 The IUPAC name of $\text{BrCH}_2-\text{CH}-\text{CO}-\text{CH}_2-\text{CH}_2\text{CH}_3$ is:



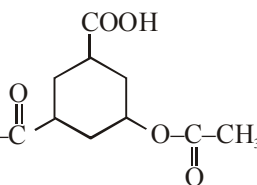
- (A) 2-Bromomethyl-3-oxohexanamide (B) 1-Bromo-2-amino-3-oxohexane
(C) 1-Bromo-2-amino-n-propyl ketone (D) 3-Bromo-2-propyl propanamide

Q.42 IUPAC name will be $\text{CH}_2-\text{CH}-\text{CH}_2$



- (A) 1,2,3-Tricyano propane (B) Propane-1,2,3- trinitrile
(C) 1,2,3-Cyano propane (D) Propane-1,2,3-tricarbonitrile

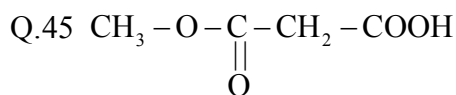
Q.43 The IUPAC name of compound $\text{CH}_3\text{O}-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{O}-\text{C}(=\text{O})-\text{CH}_3$



- (A) 3-Carbonyl methoxy -5- Ethanoyl oxy cyclohexanecarboxylic acid
(B) 3-Ethanoyl oxy -5- Methoxy carbonyl cyclohexane carboxylic acid
(C) 5-Ethanoyl oxy -5- Methoxy carbonyl cyclohexanecarboxylic acid
(D) 3-Methoxy carbonyl -5- Ethanoyl oxy cyclohexane carboxylic acid

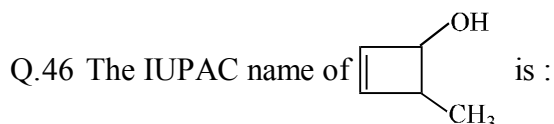
Q.44 The IUPAC name of $\text{CH}_3-\text{C}(=\text{O})-\text{O}-\text{CH}_2-\text{C}(=\text{O})-\text{OH}$ is:

- (A) 1-Acetoxy acetic acid (B) 2-Acetoxy ethanoic acid
(C) 2-Ethanoyloxyacetic acid (D) 2-Ethanoyloxyethanoic acid

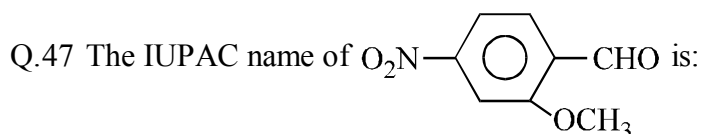


The correct IUPAC systematic name of the above compound is:

- (A) 2-Acetoxy ethanoic acid (B) 2-Methoxy carbonyl ethanoic acid
(C) 3-Methoxy formyl ethanoic acid (D) 2-Methoxy formyl acetic acid

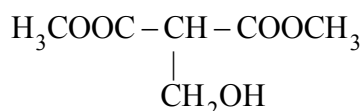


- (A) 3-Methyl cyclobut-1-ene-2-ol (B) 4-Methyl cyclobut-2-ene-1-ol
(C) 4-Methyl cyclobut-1-ene-3-ol (D) 2-Methyl cyclobut-3-ene-1-ol

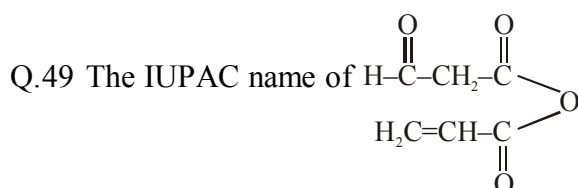


- (A) 2-Methoxy-4-nitro benzaldehyde (B) 4-Nitro anisaldehyde
(C) 3-Methoxy-4-formyl nitro benzene (D) 2-Formyl-4-nitro anisole

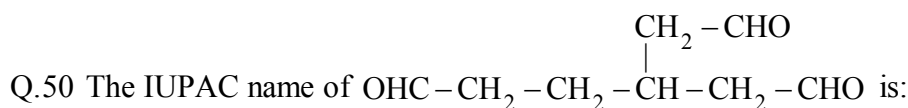
Q.48 The IUPAC name of compound



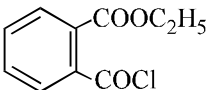
- (A) 2-(Hydroxy methyl) methyl propanedioate (B) Methyl-2-(hydroxy methyl) propanedioate
(C) 2-(Hydroxy methyl) dimethyl propanedioate (D) None of these



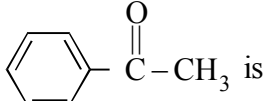
- (A) 2-Formyl ethanoic propanoic Anhydride (B) 2-Oxo-propanoic prop-2-enoic Anhydride
(C) Prop-2-enoic-2-formyl propanoic Anhydride (D) 2-Formyl ethanoic prop-2-enoic Anhydride



- (A) 4,4-Di(formylmethyl) butanal (B) 2-(Formylmethyl) butane-1, 4-dicarbaldehyde
(C) Hexane-3-acetal-1, 6-dial (D) 3-(Formylmethyl) hexane-1, 6-dial

Q.51 The IUPAC name of  is :

- (A) 2-Chlorocarbonyl ethylbenzoate
(B) 2-Carboxyethyl benzoyl chloride
(C) Ethyl-2-(chlorocarbonyl)benzoate
(D) Ethyl-1-(chlorocarbonyl)benzoate

Q.52 The IUPAC name of  is:

- (A) Phenyl ethanone
(B) Methyl phenyl ketone
(C) Acetophenone
(D) Phenyl methyl ketone

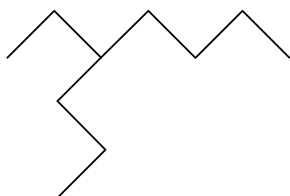
Q.53 Structural formula of isopropyl methanoate is :

- (A) $\text{CH}_3 - \underset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{O} - \underset{\text{CH}_3}{\underset{|}{\text{CH}}} - \text{CH}_3$
(B) $\text{H} - \underset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{O} - \text{CH}_2 - \underset{\text{CH}_3}{\underset{|}{\text{CH}}} - \text{CH}_3$
(C) $\text{CH}_3 - \underset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{O} - \text{CH}_2 - \underset{\text{CH}_3}{\underset{|}{\text{CH}_2}}$
(D) $\text{H} - \underset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{O} - \underset{\text{CH}_3}{\underset{|}{\text{CH}}} - \text{CH}_3$

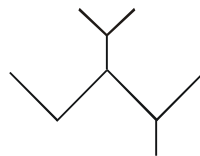
EXERCISE # II

Give the IUPAC names for each of the following :

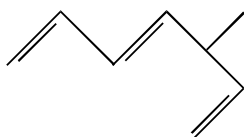
Q.1



Q.2



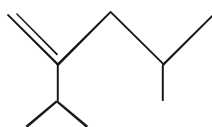
Q.3



Q.4



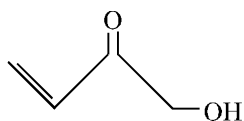
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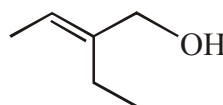
Q.6



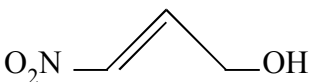
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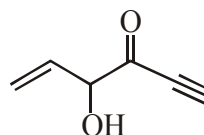
Q.8



Q.9



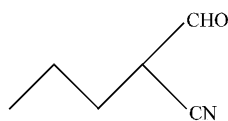
Q.10



Q.11



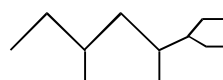
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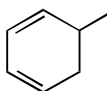
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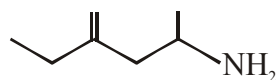
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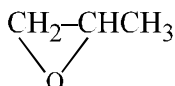
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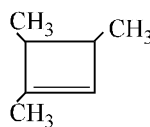
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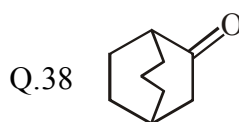
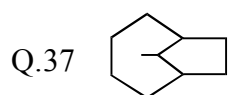
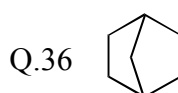
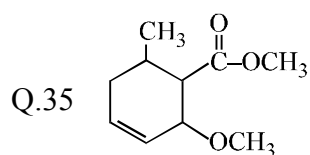
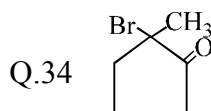
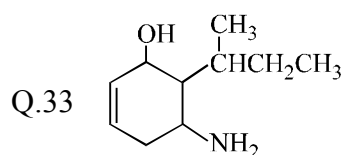
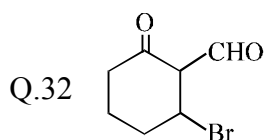
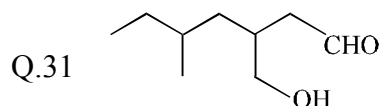
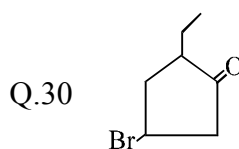
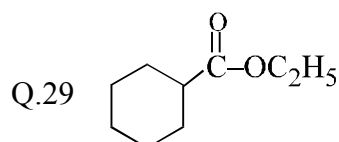
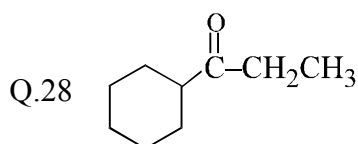
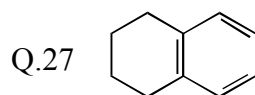
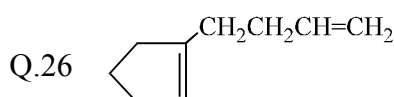
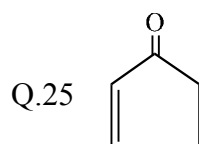
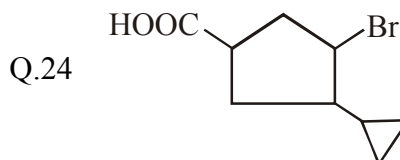
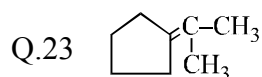
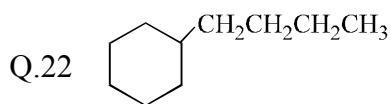
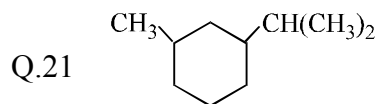
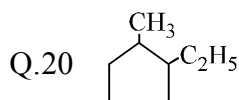
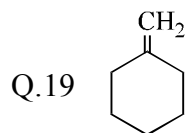


Q.17



Q.18

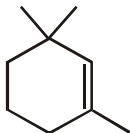




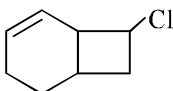
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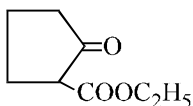
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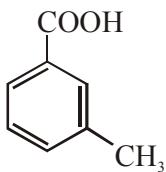
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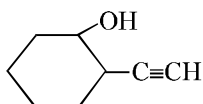
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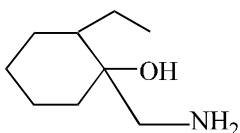
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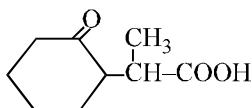
Q.49



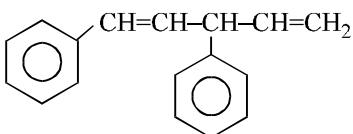
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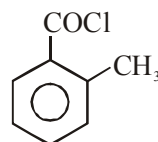
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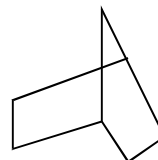
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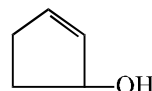
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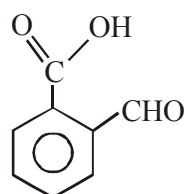
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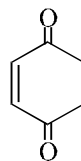
Q.44



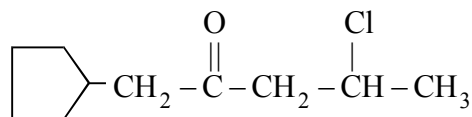
Q.46



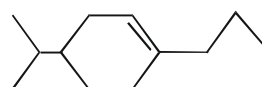
Q.48



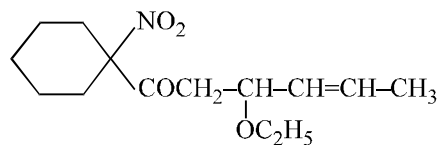
Q.50



Q.52



Q.54



EXERCISE # III

- Q.1 Which of the following pairs have absence of carbocyclic ring in both compounds?
 (A) Pyridine, Benzene (B) Benzene, Cyclohexane
 (C) Cyclohexane, Furane (D) Furane, Pyridine
- Q.2 The commercial name of trichloroethene is:
 (A) Westron (B) Perclene (C) Westrosol (D) Orlone
- Q.3 A substance containing an equal number of primary, secondary and tertiary carbon atoms is:
 (A) Mesityl Oxide (B) Mesitylene (C) Maleic acid (D) Malonic acid
- Q.4 The IUPAC name of the compound Glycerine $\text{CH}_2 - \text{CH} - \text{CH}_2$ is:
 $\begin{array}{ccc} | & | & | \\ \text{OH} & \text{OH} & \text{OH} \end{array}$
 (A) 1,2,3-Tri hydroxy propane (B) 3-Hydroxy pentane-1,5-diol
 (C) 1,2,3-Hydroxy propane (D) Propane-1,2,3-triol
- Q.5 Which of the following is crotonic acid:
 (A) $\text{CH}_2 = \text{CH} - \text{COOH}$ (B) $\text{C}_6\text{H}_5 - \text{CH} = \text{CH} - \text{COOH}$
 (C) $\text{CH}_3 - \text{CH} = \text{CH} - \text{COOH}$ (D) $\begin{array}{c} \text{CH} - \text{COOH} \\ || \\ \text{CH} - \text{COOH} \end{array}$
- Q.6 The group of heterocyclic compounds is:
 (A) Phenol, Furane (B) Furane, Thiophene
 (C) Thiophene, Phenol (D) Furane, Aniline
- Q.7 **Column - I** **Column - II**
(Common Name) **(Structural formula)**
- (A) Isooctane (P) $\begin{array}{cc} \text{CH}_2 & - & \text{CH}_2 \\ | & & | \\ \text{Cl} & & \text{Cl} \end{array}$
- (B) Neopentane (Q) $\begin{array}{ccccccc} & & \text{CH}_3 & & & & \\ & & | & & & & \\ \text{CH}_3 & - & \text{C} & - & \text{CH} & - & \text{CH} & - & \text{CH}_3 \\ & & | & & | & & \\ & & \text{CH}_3 & & \text{CH}_3 & & \end{array}$
- (C) Ethylidene chloride (Geminal dihalide) (R) $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH} - \text{CH}_3$
 $\quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad |$
 $\quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \text{CH}_3$
- (D) Ethylene Dichloride (Vicinal dihalide) (S) $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 - \text{C} - \text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$
- (T) $\text{CH}_3 - \text{CH} \begin{array}{l} \nearrow \text{Cl} \\ \searrow \text{Cl} \end{array}$

Q.8 Column - I
(Common Name)

- (A) Acetone
- (B) Acetaldehyde
- (C) Crotonaldehyde
- (D) Acrolein

Column - II
(Structural formula)

- (P) $\text{CH}_2 = \text{CH} - \overset{\text{O}}{\parallel} \text{C} - \text{H}$
- (Q) $\text{CH}_3 - \overset{\text{O}}{\parallel} \text{C} - \text{CH}_3$
- (R) $\text{CH}_3 - \text{CH} = \text{CH} - \overset{\text{O}}{\parallel} \text{C} - \text{H}$
- (S) $\text{CH}_3 - \overset{\text{O}}{\parallel} \text{C} - \text{H}$

Q.9 Column - I
(Common Name)

- (A) $\begin{array}{c} \text{CHO} \\ | \\ \text{CHO} \end{array}$
- (B) $\begin{array}{c} \text{CHO} \\ | \\ \text{H} - \text{C} - \text{OH} \\ | \\ \text{CH}_2 - \text{OH} \end{array}$
- (C) $\text{H}_2\text{N} - \text{CH}_2 - \text{COOH}$
- (D) $\begin{array}{c} \text{H} \\ | \\ \text{CH}_3 - \text{C} - \text{COOH} \\ | \\ \text{OH} \end{array}$

Column - II
(Structural formula)

- (P) Lactic acid (In milk)
- (Q) Glyoxal
- (R) Glyceraldehyde
- (S) Glycine
- (T) Glycerol

Q.10 Column - I
(Common Name)

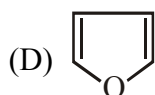
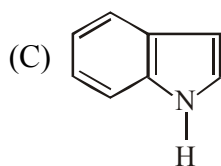
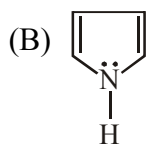
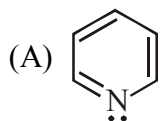
- (A) Fumaric acid
- (B) Adipic acid
- (C) Maleic acid
- (D) Tartaric acid

Column - II
(Structural formula)

- (P) $\begin{array}{c} \text{HO} - \text{CH} - \text{COOH} \\ | \\ \text{HO} - \text{CH} - \text{COOH} \end{array}$
- (Q) $\begin{array}{c} \text{HC} - \text{COOH} \\ \parallel \\ \text{HOOC} - \text{CH} \end{array}$
- (R) $\begin{array}{c} \text{H} - \text{C} - \text{COOH} \\ \parallel \\ \text{H} - \text{C} - \text{COOH} \end{array}$
- (S) $\text{COOH}(\text{CH}_2)_4\text{COOH}$

Q.11 Column - I

(Common Name)



Column - II

(Structural formula)

(P) Pyrrole

(Q) Furan

(R) Thiophene

(S) Indol

(T) Pyridine

Q.12 Column - I

(Common Name)

(A) p-Cresol

(B) p-Xylene

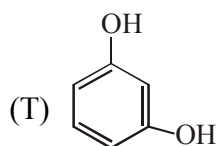
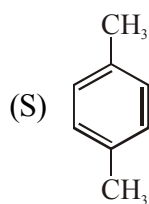
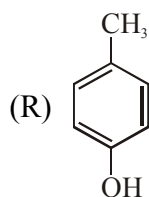
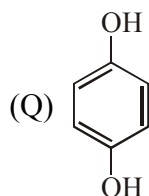
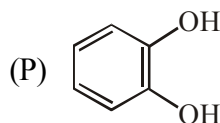
(C) Resorcinol

(D) Quinol

(E) Catechol

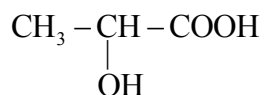
Column - II

(Structural formula)

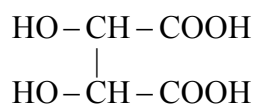


Q.13 Which of the following is not correctly matched:

(A) Lactic acid



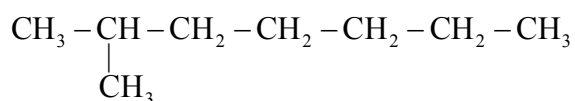
(B) Tartaric acid



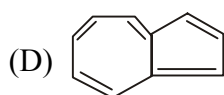
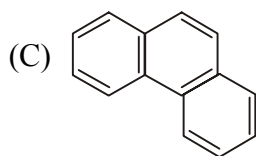
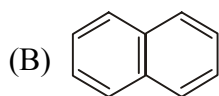
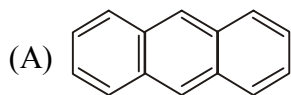
(C) Pivaldehyde



(D) Iso-octane



Q.14 **Column - I**



Column - II

(P) Phenanthrene

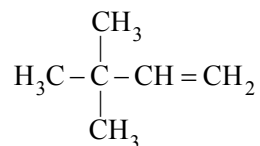
(Q) Anthracene

(R) Azulene

(S) Napthalene

EXERCISE # IV

- Q.1 The IUPAC name of the compound having the formula is : [JEE 1984]



- (A) 3,3,3-trimethyl-1-propene
(B) 1,1,1-trimethyl-2-propene
(C) 3,3-dimethyl-1-butene
(D) 2,2-dimethyl-3-butene

- Q.2 Write the IUPAC name of $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}\cdot\text{COOH}$ [JEE 1986]

- Q.3 The IUPAC name of the compound $\text{CH}_2=\text{CH}-\text{CH}(\text{CH}_3)_2$ is :

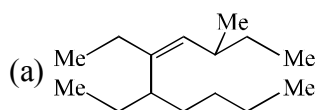
- (A) 1,1-dimethyl-2-propene (B) 3-methyl-1-butene
(C) 2-vinyl propane (D) None of the above

[JEE 1987]

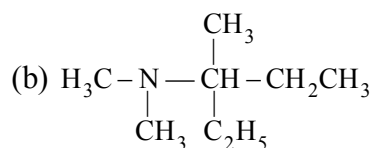
- Q.4 The number of sigma and pi-bonds in 1-butene 3-yne are: [JEE 1989]

- (A) 5 sigma and 5 pi (B) 7 sigma and 3 pi
(C) 8 sigma and 2 pi (D) 6 sigma and 4 pi

- Q.5 Write I.U.P.A.C name of following :



Me = methyl group



[JEE 1990]

- Q.6 Write IUPAC name of succinic acid. [JEE 1994]

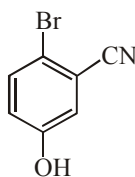
- Q.7 The IUPAC name of $\text{C}_6\text{H}_5\text{COCl}$ is

- (A) Benzoyl chloride
(B) Benzene chloro ketone
(C) Benzene carbonyl chloride
(D) Chloro phenyl ketone

[JEE 2006]

Q.8 The IUPAC name of the following compound is

[JEE 2009]



(A) 4-Bromo-3-cyanophenol

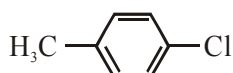
(B) 2-Bromo-5-hydroxybenzonitrile

(C) 2-Cyano-4-hydroxybromobenzene

(D) 6-Bromo-3-hydroxybenzonitrile

Q.9 The IUPAC name(s) of the following compound is(are) :

[JEE 2017]



(A) 4-methylchlorobenzene

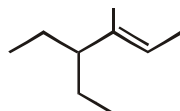
(B) 4-chlorotoluene

(C) 1-chloro-4-methylbenzene

(D) 1-methyl-4-chlorobenzene

10. The IUPAC name of the following compound is :

[JEE Mains On_line 2018]



(A) 4-methyl-3-ethylhex-4-ene

(B) 4,4-diethyl-3-methylbut-2-ene

(C) 3-ethyl-4-methylhex-4-ene

(D) 4-ethyl-3-methylhex-2-ene

ANSWER KEY**EXERCISE # I**

Q.1	B	Q.2	B	Q.3	D	Q.4	D	Q.5	C	Q.6	B	Q.7	A
Q.8	D	Q.9	A	Q.10	A	Q.11	A	Q.12	B	Q.13	D	Q.14	C
Q.15	B	Q.16	C	Q.17	D	Q.18	B	Q.19	A	Q.20	B	Q.21	C
Q.22	B	Q.23	B	Q.24	D	Q.25	C	Q.26	D	Q.27	D	Q.28	C
Q.29	B	Q.30	B	Q.31	B	Q.32	B	Q.33	B	Q.34	D	Q.35	C
Q.36	B	Q.37	C	Q.38	C	Q.39	B	Q.40	C	Q.41	A	Q.42	D
Q.43	B	Q.44	D	Q.45	B	Q.46	B	Q.47	A	Q.48	B	Q.49	D
Q.50	D	Q.51	C	Q.52	A	Q.53	D						

EXERCISE # II

Q.1	4-Ethyl octane	Q.17	1,2-epoxy propane
Q.2	3-Ethyl-2,4-dimethyl pentane	Q.18	1,3,4-trimethyl cyclobutene
Q.3	5-Methyl hepta-1,3,6-triene	Q.19	Methylene cyclohexane
Q.4	Hepta-1,5-dien-3-yne	Q.20	1-ethyl-2-methylcyclopentane
Q.5	2-Isopropyl-4-methyl pent-1-ene or 4-Methyl-2-(methyl ethyl) pent-1-ene	Q.21	1-methyl-3-(methyl ethyl) cyclohexane or 1-isopropyl-3-methylcyclohexane
Q.6	3-Methoxypropene	Q.22	Butyl cyclohexane
Q.7	1-Hydroxybut-3-en-2-one	Q.23	Isopropylidenecyclopentane or 1-methyl ethylidene cyclopentane
Q.8	2-Ethylbut-2-en-1-ol	Q.24	3-Bromo-4-cyclopropyl cyclopentane carboxylic acid
Q.9	3-nitroprop-2-en-1-ol	Q.25	Cyclopent-2-en-1-one
Q.10	4-hydroxyhex-5-en-1-yn-3-one	Q.26	1-(3-butenyl) cyclopentene
Q.11	4,6-Bis-[1,1-Dimethyl ethyl] Nonane	Q.27	1,2-diethenyl cyclohexene
Q.12	2-Formyl pentane nitrile	Q.28	1-cyclohexyl-1-propanone
Q.13	2,2,6,7-tetramethyloctane	Q.29	Ethyl cyclohexanecarboxylate
Q.14	3-Ethyl-4,6-dimethyloctane	Q.30	4-Bromo-2-ethyl cyclopentanone
Q.15	5-Methyl cyclohexa-1,3-diene	Q.31	3-(hydroxymethyl)-5-methylheptanal
Q.16	4-Ethyl Pent-4-en-2-amine		

EXERCISE # III

- Q.1 D Q.2 C Q.3 B Q.4 D Q.5 C Q.6 B
- Q.7 (A)-Q ; (B)-S ; (C)-T ; (D)-P Q.8 (A)-Q ; (B)-S ; (C)-R ; (D)-P
- Q.9 (A)-Q ; (B)-R ; (C)-S ; (D)-P Q.10 (A)-Q ; (B)-S ; (C)-R ; (D)-P
- Q.11 (A)-T ; (B)-P ; (C)-S ; (D)-Q Q.12 (A)-R ; (B)-S ; (C)-T ; (D)-Q ; (E)-P
- Q.13 D Q.14 (A)-Q ; (B)-S ; (C)-P ; (D)-R

EXERCISE # IV

- Q.1 C
- Q.2 $\text{CH}_3 - \text{CH}_2 - \text{CH} = \text{CH} - \text{COOH}$
 5 4 3 2 1
 2-pentene-1-oic acid and or 2-pentenoic acid
- Q.3 B Q.4 B
- Q.5 (a) 5,6-diethyl-3-methyl-dec-4-ene
 (b) N,N, 3-trimethyl-3-pentanamine
- Q.6 Butane-1,4-dioic acid Q.7 C Q.8 B Q.9 B,C
10. D

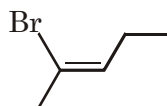
Important Notes

[illegible]

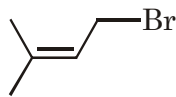
STEREO ISOMERISM

EXERCISE # I (MAINS ORIENTED)

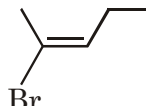
- 1.** Which one of the following statements concerning compounds **V–Z** is true :



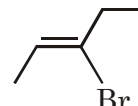
(V)



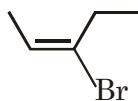
(W)



(X)



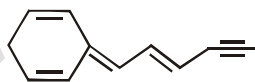
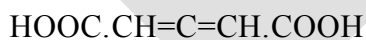
(Y)



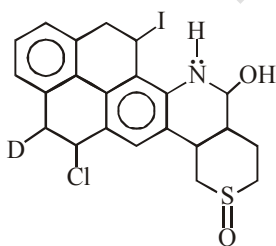
(Z)


- (A) **V** and **X** are conformational isomers
(B) **Y** and **Z** are constitutional isomers
(C) **X** and **Y** are constitutional isomers
(D) **V** and **Y** are stereoisomers
2. Which of the following compound has no isomer?
(A) $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$
(B) CH_3CHO
(C) $\text{CH}_2=\text{CH}-\text{Cl}$
(D) $\text{ClCH}_2\text{CH}_2\text{Cl}$
3. Compound CH_2Cl_2 contain :
(A) Plane of symmetry
(B) Centre of symmetry
(C) Axis of symmetry
(D) Both (A) & (C)
4. Number of POS present in CH_4 :
(A) 3
(B) 4
(C) 5
(D) 6
5. How many stereoisomers of the following molecule are possible ?
$$\text{HOOC}.\text{CH}=\text{C}=\text{CH}.\text{COOH}$$

(A) Two optical isomers
(B) Two geometrical isomers
(C) Two optical and two geometrical isomers
(D) None
6. The number of cis-trans isomer possible for the following compound.

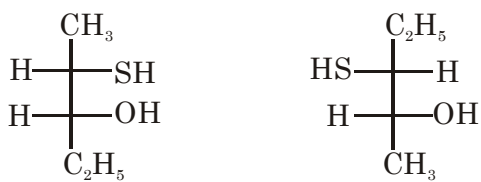


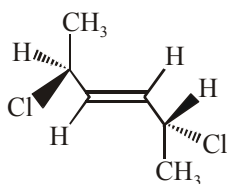
- (A) 2 (B) 4 (C) 6 (D) 8



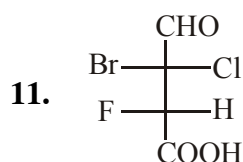
7.  has 'x' chiral centre then find the value of x :

- (A) 7 (B) 8 (C) 6 (D) 5

8. 
- (A) Diastereomers (B) Enantiomers (C) Identical (D) Constitutional isomers
9. The number of optically active compounds in the isomers of C_4H_9Br is :
- (A) 1 (B) 2 (C) 3 (D) 4
10. Compound have :

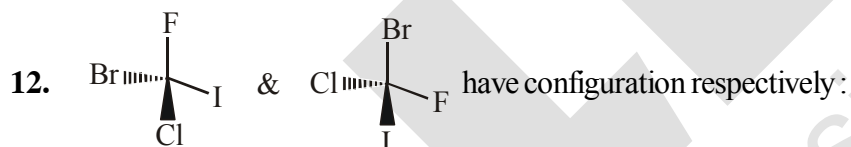


- (A) Plane of symmetry (B) Centre of symmetry
(C) Axis of symmetry (D) None



Configuration of compound is :

- (A) 2S, 3S (B) 2R, 3S (C) 2R, 3R (D) 2S, 3R

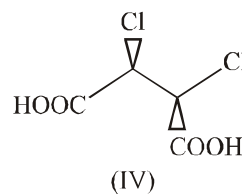
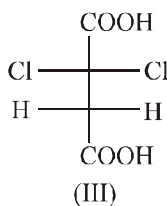
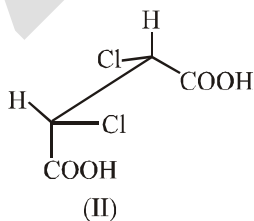
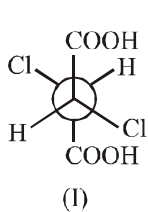


- (A) R, S (B) S, S (C) S, R (D) R, R

13. Minimum molecular weight of a hydrocarbon containing minimum number of C-atom to show optical isomerism :

- (A) 100 (B) 80 (C) 68 (D) 70

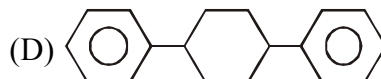
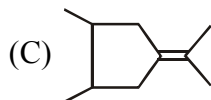
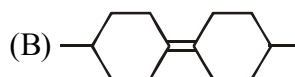
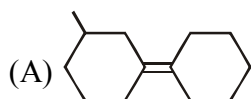
14. For the given configuration :



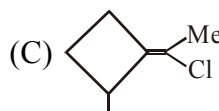
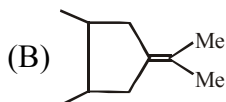
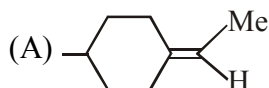
Which of the compound/configuration are optically active :

- (A) I (B) II (C) III (D) IV

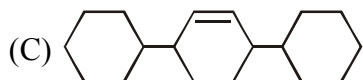
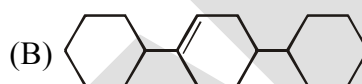
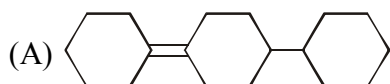
16. Which of the following will not show optical isomerism :



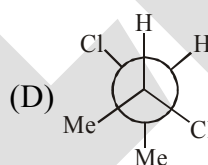
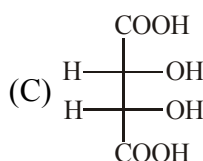
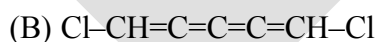
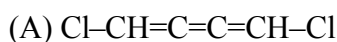
16. Which of the following will not show optical isomerism :



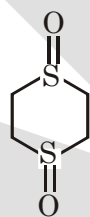
17. Optical & geometrical isomerism both can be shown by :-



18. Which of the following will not show optical isomerism :



19. The correct statement for the given compound is



(A) It can shows geometrical isomerism

(B) It can show optical isomerism

(C) It contain chiral centre

(D) None of these

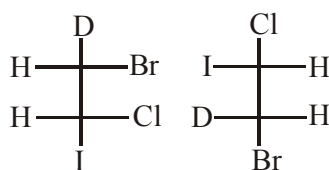
20. Meso-tartaric acid and d-tartaric acid are :-

(A) Positional isomers (B) Enantiomers

(C) Diastereomers

(D) Racemic mixture

21. The two compounds given below are :

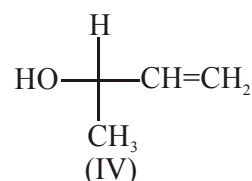
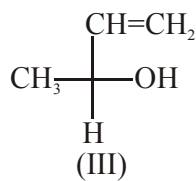
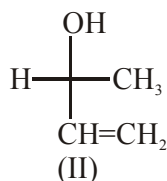
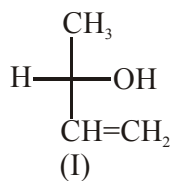


(A) Enantiomers

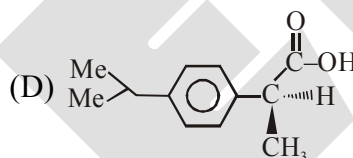
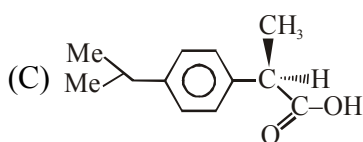
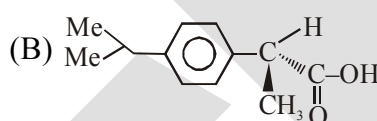
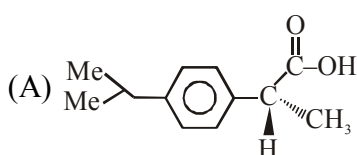
(B) Diastereomers

(C) Optically inactive (D) Identical

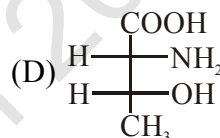
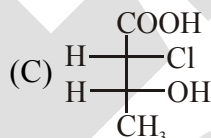
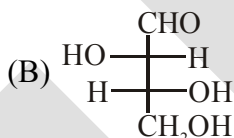
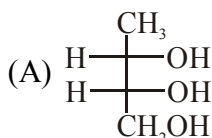
22. Which of the following combinations amongst the four Fischer projections represents the same absolute configurations ?



- (A) (II) and (III) (B) (I) and (IV) (C) (II) and (IV) (D) (III) and (IV)
23. The S-ibuprofen is responsible for its pain relieving property. Which one of the structure shown is S-ibuprofen :



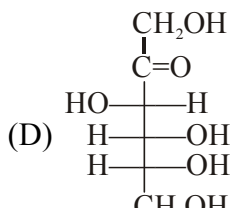
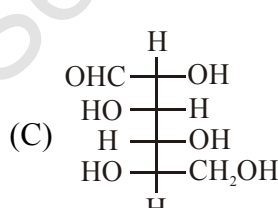
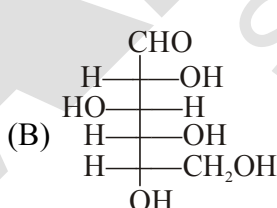
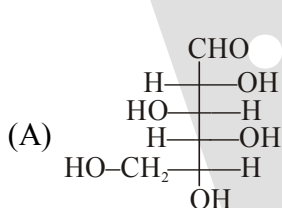
24. Which of the following is a 'threo' isomer :



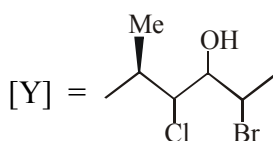
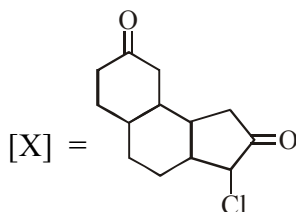
25. Number of possible stereoisomers of glucose are :-

- (A) 10 (B) 8 (C) 16 (D) 20

26. Which of the following is not D sugar :

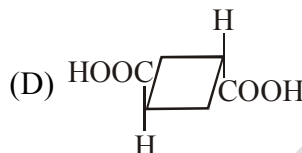
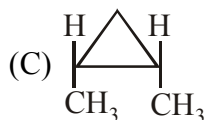
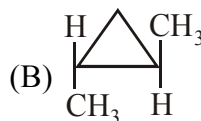
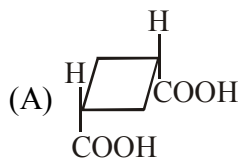


27. Number of chiral centres in [X] & [Y] is a & b respectively. The value of (a-b) is :

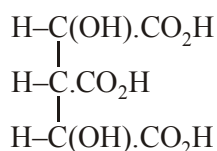


- (A) 1 (B) 2 (C) 3 (D) 4

28. Which one of the following is resolvable :



29. How many stereoisomers can exist for the following acid.



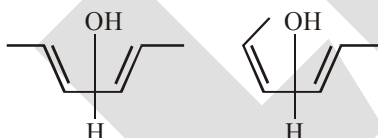
(A) Two

(B) Four

(C) Eight

(D) Six

30. Incorrect relationship between given compounds are



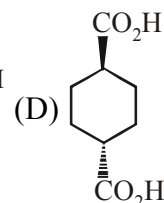
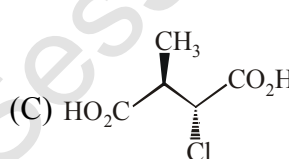
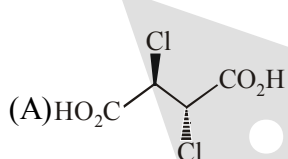
(A) Both are geometrical isomers

(B) Both are stereo isomers

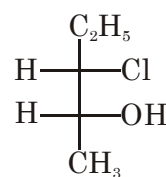
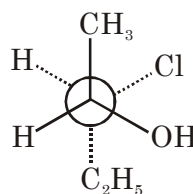
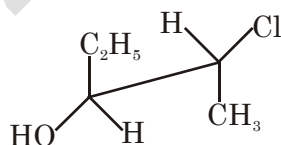
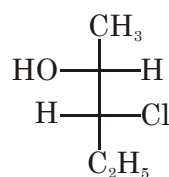
(C) Both are enantiomers

(D) Both are diastereomers

31. Identify meso compound.



32. The two projection formulae that represent a pair of enantiomers are :-



(I)

(II)

(III)

(IV)

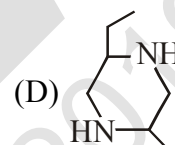
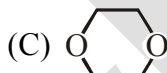
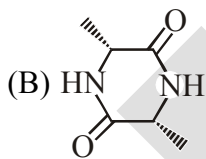
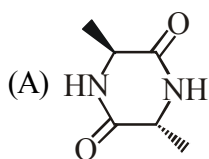
(A) I and II

(B) III and IV

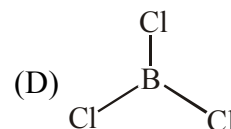
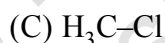
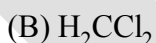
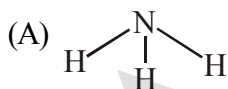
(C) I and III

(D) II and IV

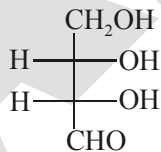
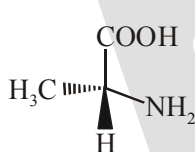
33. A pure sample of 2-chlorobutane shows rotation of PPL by 30° in standard conditions. When above sample is made impure by mixing its opposite form, so that the composition of the mixture becomes 87.5% d-form and 12.5% *l*-form, then what will be the observed rotation for mixture.
- (A) -22.5° (B) $+22.5^\circ$ (C) $+7.5^\circ$ (D) -7.5°
34. When an optically active compound is placed in a 10 dm tube is present 20 gm in a 200 ml solution rotates the PPL by 30° . Calculate the angle of rotation & specific angle of rotation if above solution is diluted to 1 Litre.
- (A) 16° & 36° (B) 6° & 30° (C) 3° & 30° (D) 6° & 36°
35. Identify % optical purity if 6 gm (+)-2-butanol is mixed with 2 gm (-)-2-butanol.
- (A) 50 % (B) 66.6 % (C) 33.3 % (D) 75 %
36. A mixture of d and *l*, 2-bromobutane contain 75% d-2-bromobutane. Calculate enantiomeric excess.
- (A) 75% (B) 25% (C) 50% (D) 100%
37. Which of the following is example of meso compound?



38. Which of the following has C_2 & C_3 axis of symmetry ?



39. Configuration of I & II respectively will be :

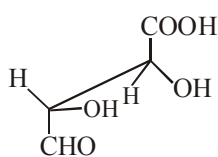
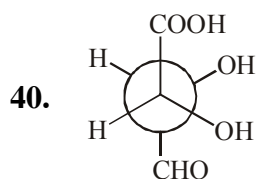


(A) D, D

(B) L, D

(C) D, L

(D) L, L



, compound related as :

(A) Enantiomers

(B) Conformation

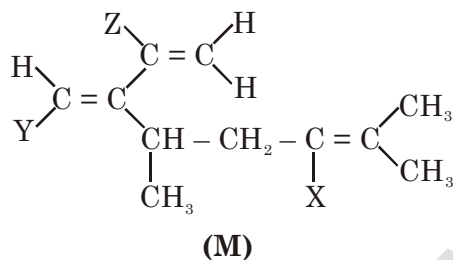
(C) Identical

(D) Diastereomers

EXERCISE # II (JEE-ADVANCE ORIENTED LEVEL-I)

Single correct Option Type :

- Molecular formula $C_5H_{10}O$ can have :
 (A) 6-Aldehyde, 4-Ketone
 (B) 5-Aldehyde, 3-Ketone
 (C) 4-Aldehyde, 3-Ketone
 (D) 5-Aldehyde, 2-Ketone
- In the given halogenoalkene M, atoms X, Y and Z represents hydrogen or bromine or chlorine. To show cis-trans isomerism, what could be the identities of atoms X, Y and Z?



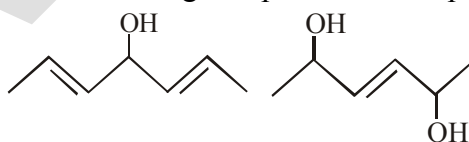
	X	Y	Z
1	Cl	H	Br
2	H	Br	Cl
3	Cl	Br	H

- (A) 1, 2 and 3 (B) 1 and 2 only (C) 2 and 3 only (D) 1 and 3 only

- Statement-1 :** is a chiral resolvable molecule.

Statement-2 : is non-superimposable on its mirror image.

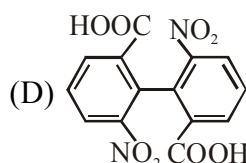
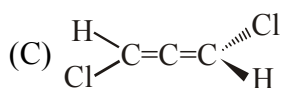
- (A) Statement-1 is true, Statement-2 is true; Statement-2 is not the correct explanation of Statement-1
 (B) Statement-1 is true, Statement-2 is true ; Statement-2 is the correct explanation of Statement-1
 (C) Statement-1 is true, Statement-2 is false
 (D) Statement-1 is false, Statement-2 is true
- Total number of stereoisomer of following compounds are respectively :-



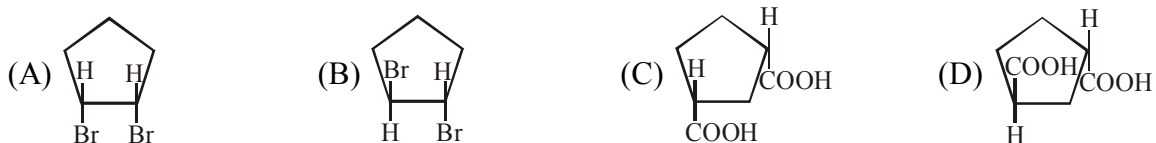
- (A) 4, 6 (B) 8 (C) 6, 6 (D) 8, 8

- Which of the following compounds are optically active ?

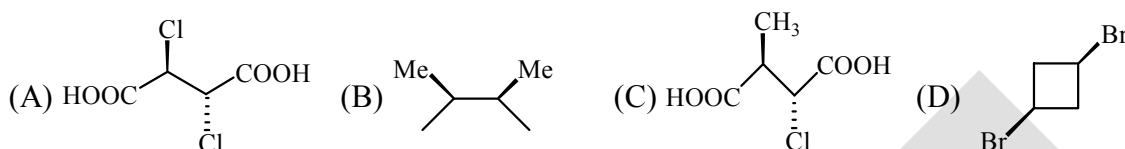
- (A) $CH_3.CHOH.CH_2.CH_3$ (B) $H_2C=CH.CH_2.CH=CH_2$



6. Which out the following are Non-resolvable :



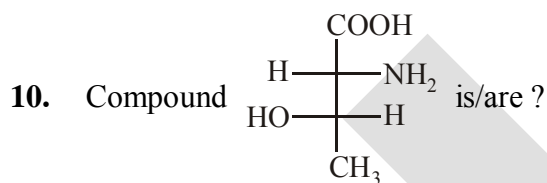
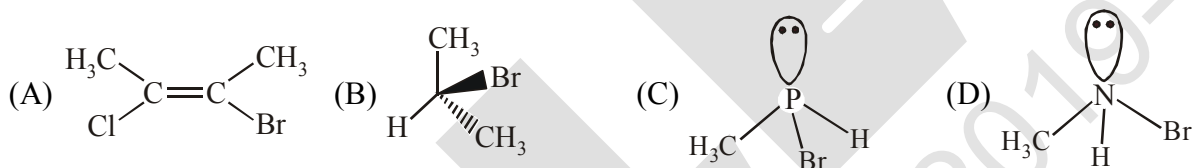
7. Identify compound(s) which is/are not meso :



8. Which of the following statements for a meso compound is/are correct :

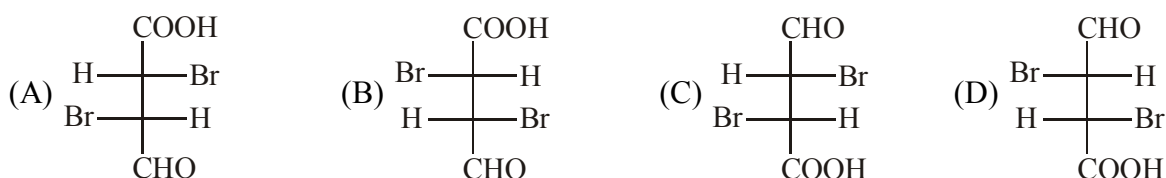
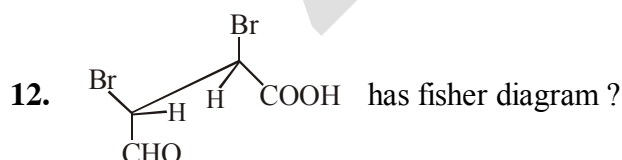
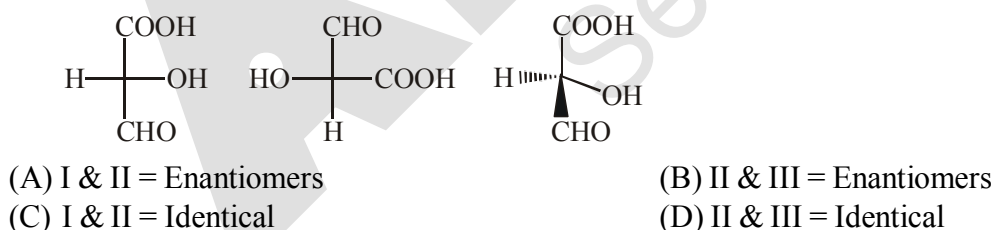
- (A) The meso compound has either a plane or centre of symmetry
 (B) The meso compound is optically inactive due to internal compensation.
 (C) The meso compound is achiral
 (D) The meso compound is formed when equal amounts of two enantiomers are mixed

9. Among the following the non-resolvable compound is/are :

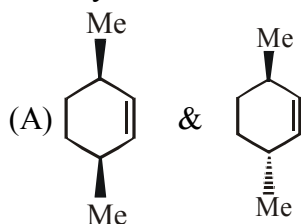


- (A) (2R, 3S), L (B) L, Erythro (C) Threo, D (D) (2R, 3S), D

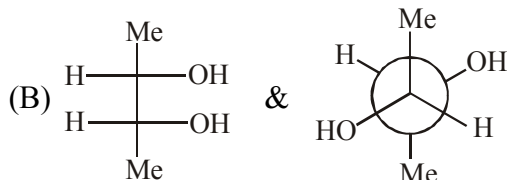
11. Relation between compounds are :



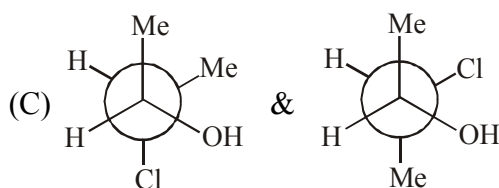
13. Identify correct relation between pair of compounds ?



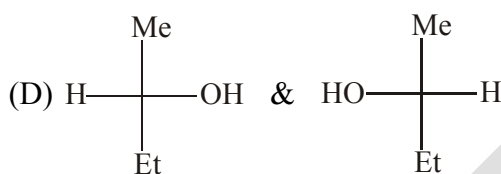
Diastereomers



Identical

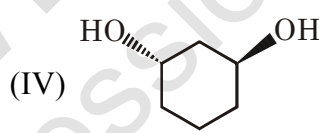
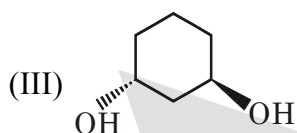
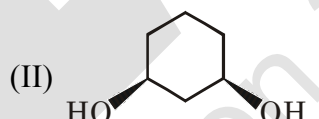
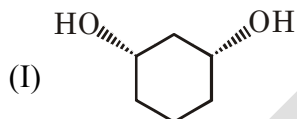


Diastereomers



Enantiomers

14. Which two of the following compounds represents a pair of enantiomers?



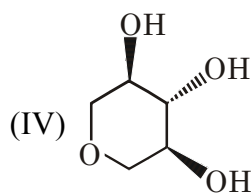
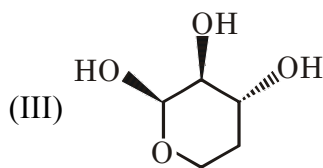
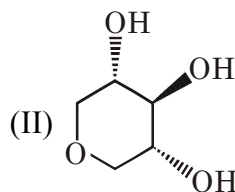
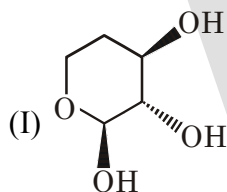
(A) I & II

(B) II & III

(C) III & IV

(D) II & IV

15. Which two of the following compounds are diastereomers?



(A) I & II

(B) II & IV

(C) III & IV

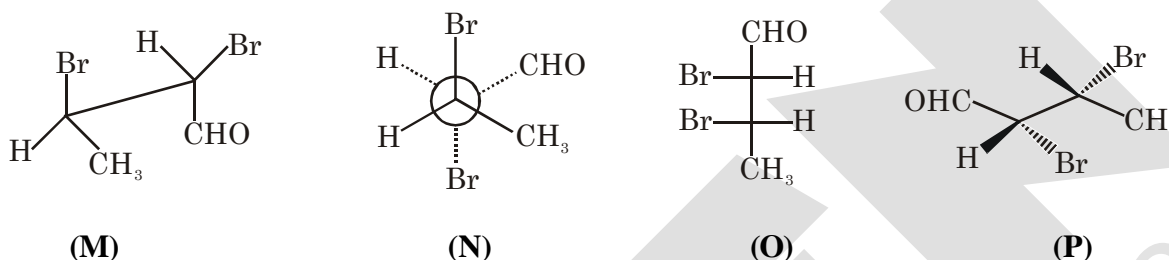
(D) I & III

16. The correct relation between the following compounds is :



- (A) Enantiomers
(B) Diastereomers
(C) Homomers (Identical)
(D) Constitutional isomers

17. Identify the correct statement regarding following molecules?



- (A) **M** and **O** are diastereomers
(B) **N** and **P** are enantiomers
(C) **M** and **N** are identical
(D) **O** and **P** are diastereomers

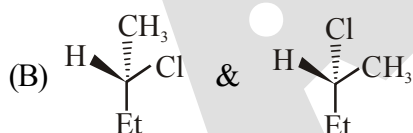
Matrix Match Type :

18. Column I

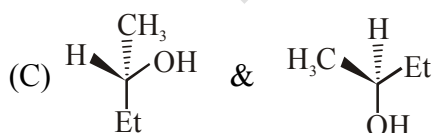
Column II



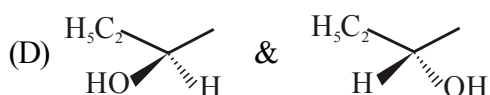
(P) Structural



(Q) Identical

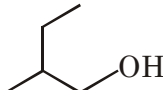
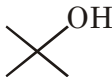
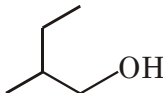



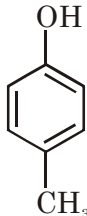
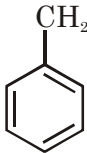


(R) Enantiomers

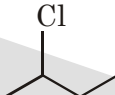
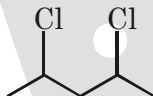
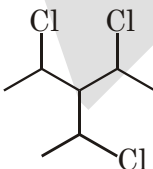
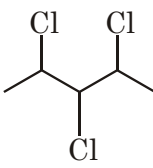


(S) Diastereomers

19. Match the column :-

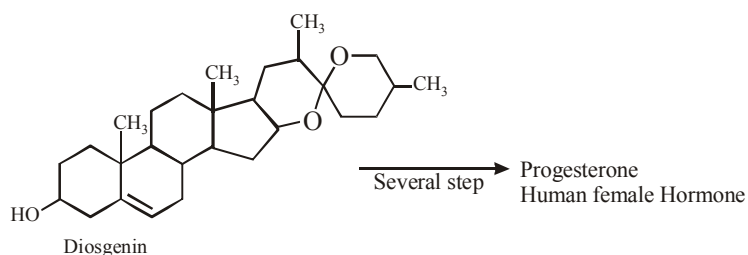
	Column-I		Column-II
(1)	 & 	(P)	Position isomers
(2)	 & 	(Q)	Chain isomers
(3)	 & 	(R)	Homologues
(4)	 & 	(S)	Functional isomers

20. Match the column :-

Column-I (Compounds)		Column-II (Total number of stereoisomers)	
(1)		(P)	8
(2)		(Q)	4
(3)		(R)	3
(4)		(S)	2

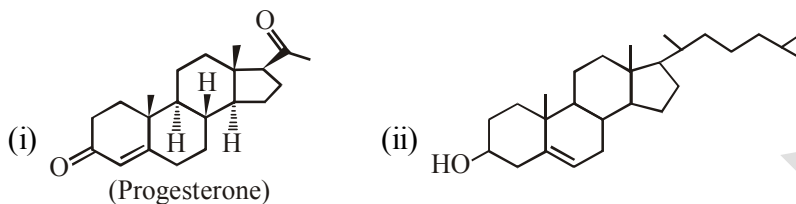
Subjective Type :

21.



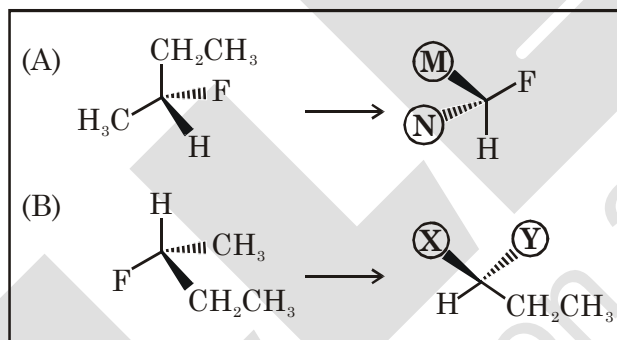
What is number of chiral centres present in Diosgenin is :

22. Calculate the total number of chiral carbon atoms in.

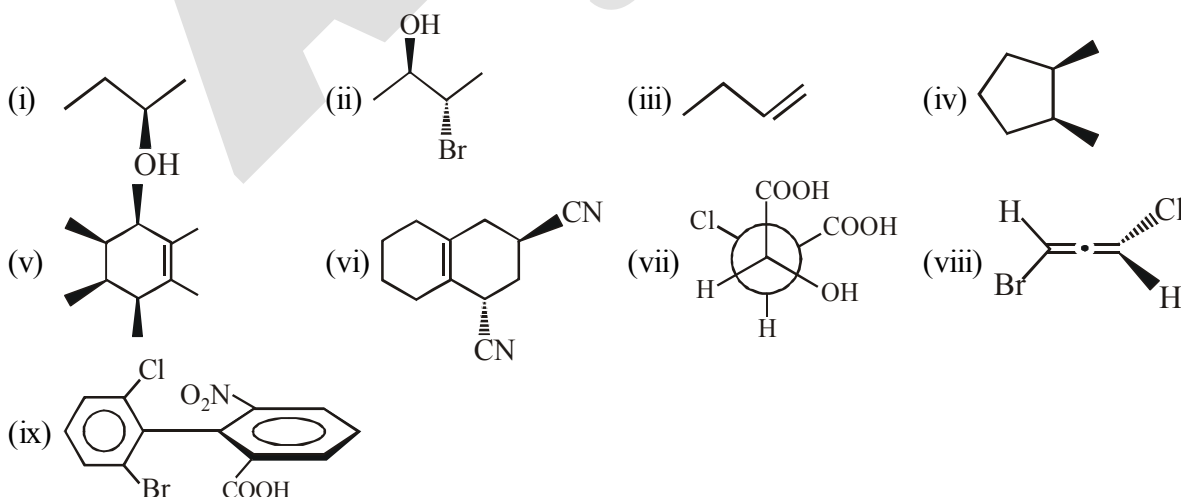


23. Total number of isomeric (including stereo) bromochlorofluoroiodo propadiene.

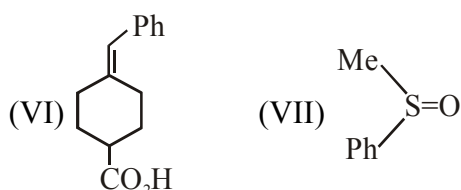
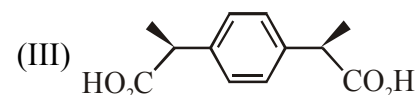
24. Re-orient the molecule at the left to match the partially drawn perspective at the right. Find the two missing substituents at their correct positions.

(A) $M = CH_3CH_2 -$
 $N = CH_3 -$ (B) $X = CH_3 -$
 $Y = F -$ (C) $M = CH_3 -$
 $N = CH_3CH_2 -$ (D) $X = F -$
 $Y = CH_3 -$ 25. Find out the total number of cyclic isomers of C_6H_{12} which are optically active ?

26. How many of the given compounds are chiral :

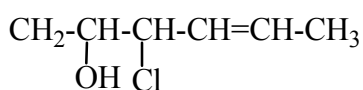


28. How many cyclopentane structures (including stereo) are possible for C_7H_{14} ?

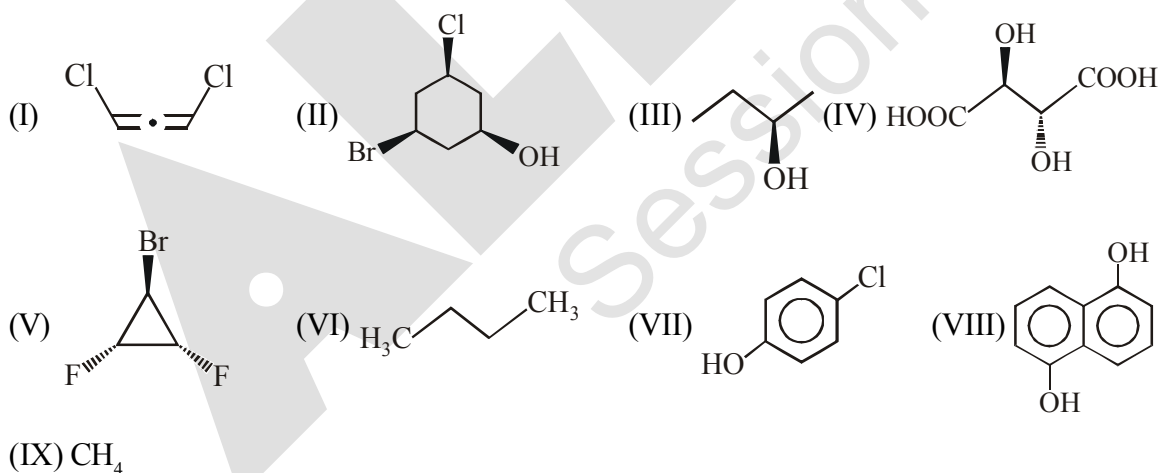


29. The number of diastereoisomers (excluding enantiomers) for 1-bromo-2-chloro-3-iodocyclopropane.

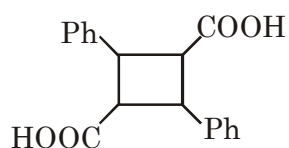
30. Identify total number of stereoisomers for the following compound :



31. How many of the given molecule / species are chiral :



32. Total geometrical isomers possible for :

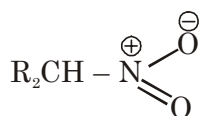


- (A) 3 (B) 4 (C) 5 (D) 8

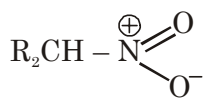
EXERCISE # III (JEE-ADVANCE ORIENTED LEVEL # II)

Single Correct Type :

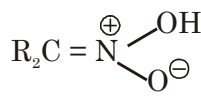
1. The correct statements describing the relationship between :



(X)

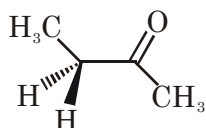


(Y)

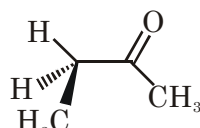


(Z)

- (A) X and Y are resonance structures and Z is a tautomer
 (B) X and Y are tautomers and Z is resonance structure
 (C) X, Y and Z are all resonance structures
 (D) X, Y and Z all are tautomers
2. The correct statements about conformations X and Y of 2-butanone are :

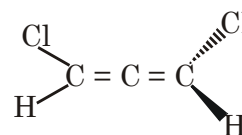
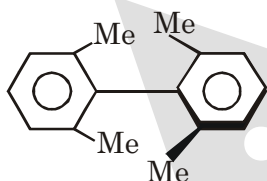
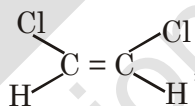
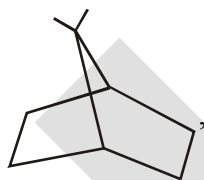
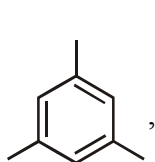


(X)

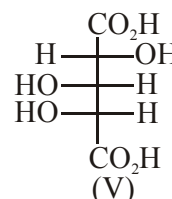
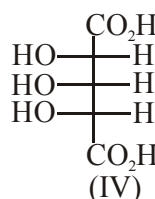
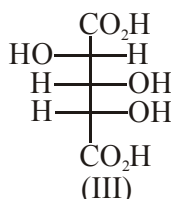
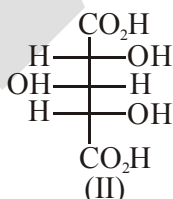
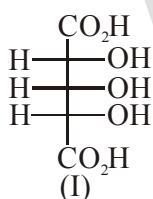


(Y)

- (a) X is more stable than Y
 (b) Y is more stable than X
 (c) Methyl groups in X are anti
 (d) Methyl groups in Y are gauche
 (A) a and d
 (B) a and c
 (C) b and c
 (D) a, c and d
3. Among the following, the number of molecules that possess C_2 -axis of symmetry is :

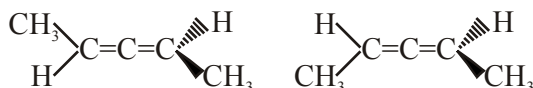


4. Observe the given compounds and answer the following questions.



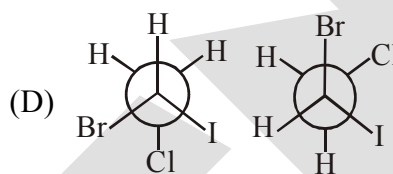
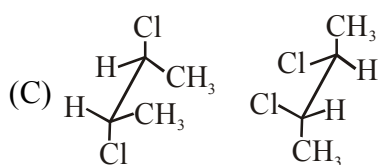
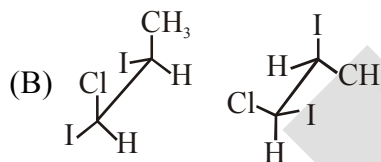
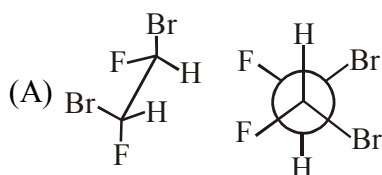
- (i) Which of the above formulae represent identical compounds ?
 (A) I and II
 (B) I and IV
 (C) II and IV
 (D) III and IV
- (ii) Which of the above compounds are enantiomers ?
 (A) II and III
 (B) III and IV
 (C) III and V
 (D) I and V

5. Which of the following option is correct regarding the given compounds :



- (A) Both are identical (B) Both are optically inactive
(C) Both are enantiomers (D) Geometrical isomer

6. Which of the following pairs of compound is/are identical ?

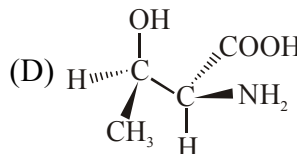
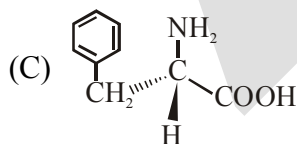
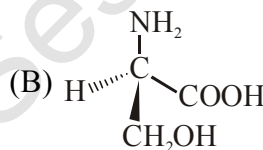
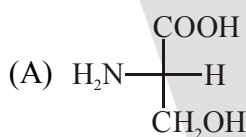


Multiple Correct Type :

7. Which of the following statements is/are not correct for D-(+) glyceraldehyde :

- (A) The symbol D indicates the dextrorotatory nature of the compound
- (B) The sign(+) indicates the dextrorotatory nature of the compound
- (C) The symbol D indicates that (–OH) group lies left to the chiral centre in the conventionally correct Fischer projection diagram
- (D) The symbol D indicates that (–OH) group lies right to the chiral centre in the conventionally correct Fischer projection diagram

8. Which of the following are correct representation of L-amino acids :



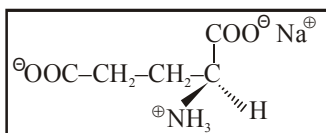
9. Identify relation between these two compounds :



- (A) Homomers (B) Enantiomers (C) Diastereomers (D) Positional Isomers

Paragraph for Question 15 to 17

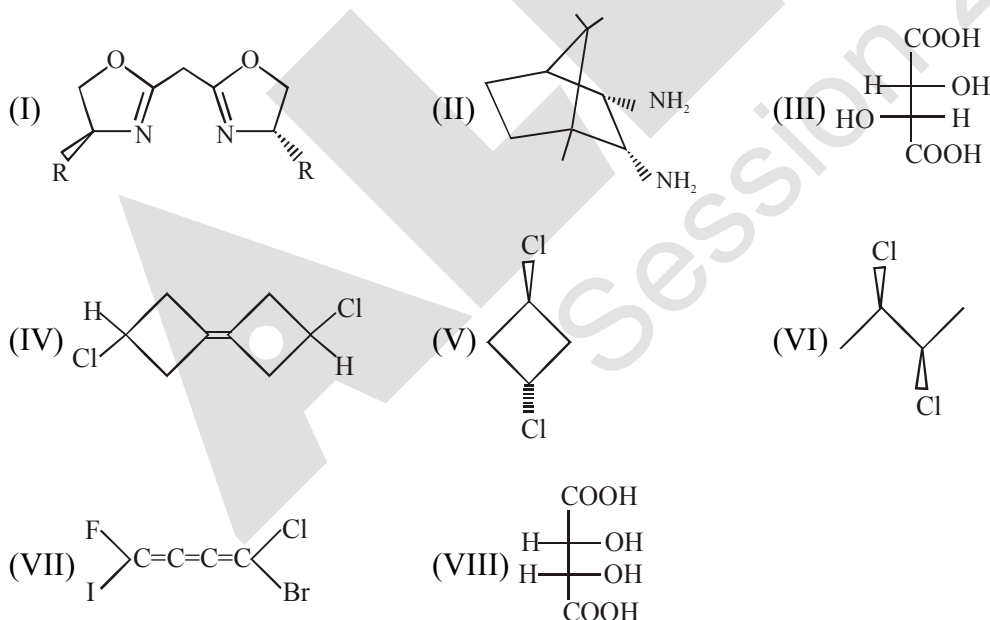
S(+) Mono sodium Glutamate (MSG) is a flavour enhancer used in many foods. Fast foods often contain substantial amount of MSG and is widely used in Chinese food. If one mole of above MSG was placed in 845 ml solution and passed through 200 mm tube, the observed rotation was found to be $+9.6^\circ$.



15. Find out the specific rotation of (–) MSG :
 (A) $+24^\circ$ (B) $+56.8^\circ$ (C) -48° (D) None of these
16. Find out the approximate percentage composition of (–) MSG in a mixture containing (+) MSG and (–) MSG whose specific optical rotation is -20° :
 (A) 83.3% (B) 16.7% (C) 91.6% (D) 74%
17. If 33.8 g of (+) MSG was put in 338 ml solution and was mixed with 16.9g of (–) MSG put in 169 ml solution and the final solution was passed through 400 mm tube. Find out observed rotation of the final solution :
 (A) $+1.6^\circ$ (B) $+4.8^\circ$ (C) $+3.2^\circ$ (D) None of these

Paragraph for Q.18 to Q.19

Among the following structures ?

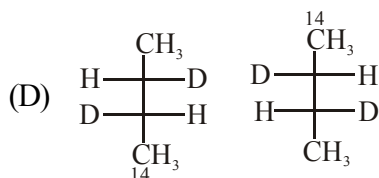
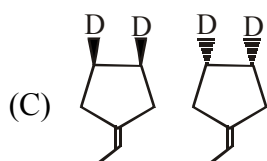
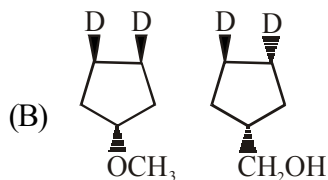
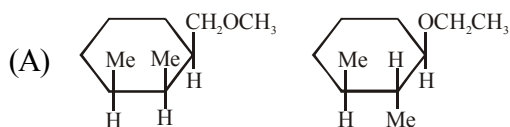


18. Optically active compound is -
 (A) III (B) IV (C) V (D) VII
19. Which of the following will not show optical isomerism -
 (A) I (B) II (C) V (D) VIII

Matrix Match Type :

20. Column-I

(Compounds)



Column-II

(Relation)

(P) Metamers

(Q) Functional Isomer

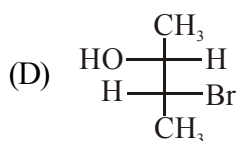
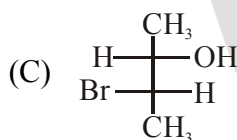
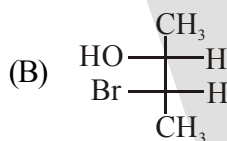
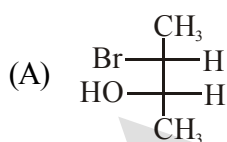
(R) Geometrical isomer

(S) Enantiomer

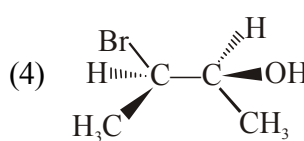
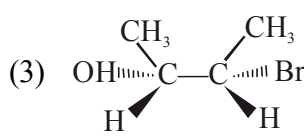
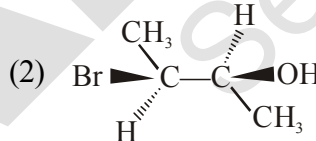
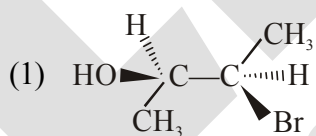
(T) Diastereomer

21. Match List-I, II, III with each other :

List - I



List - II



List - III

(i) (2R, 3R)

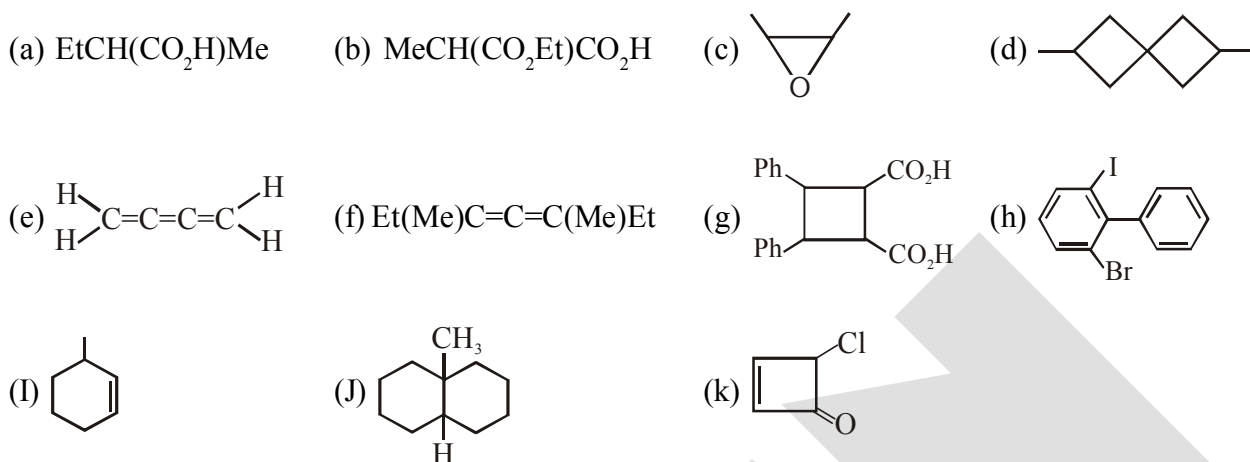
(ii) (2S, 3S)

(iii) (2S, 3R)

(iv) (2R, 3S)

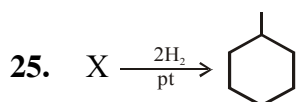
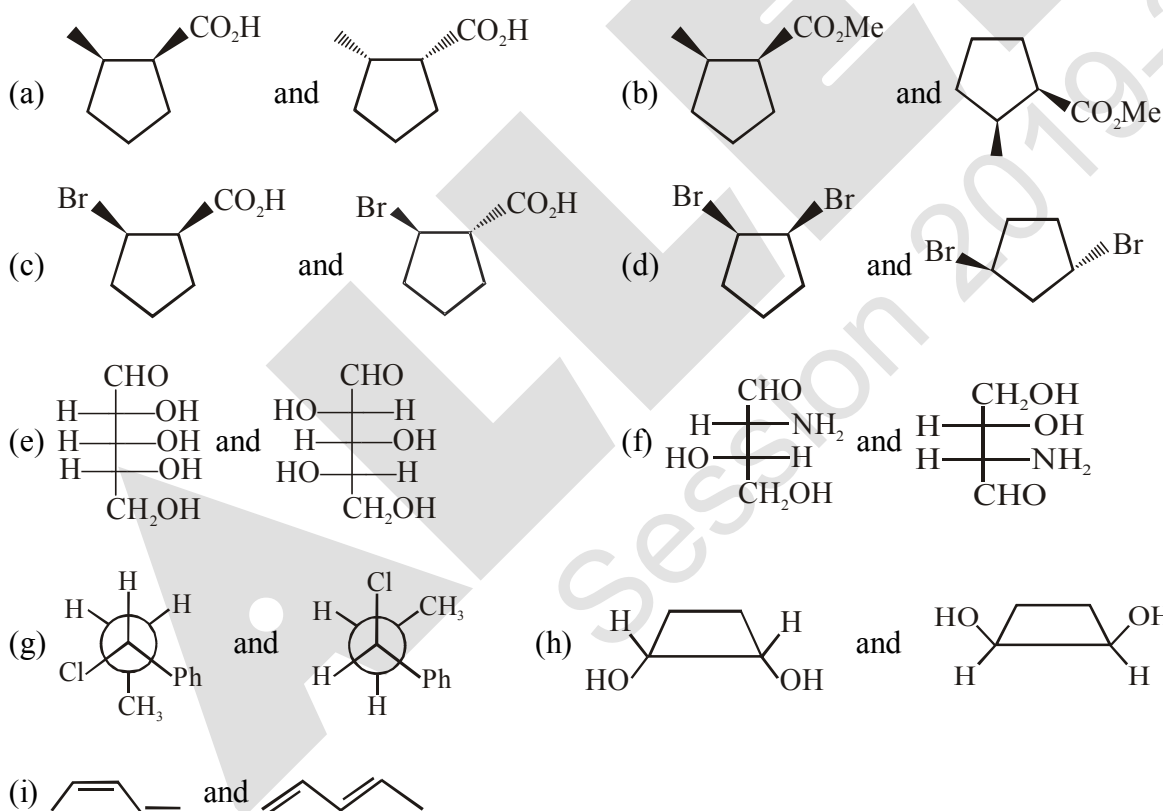
Subjective Type :

22. In what stereoisomeric forms would you expect the following compounds to exist ?



23. Calculate the number of Benzenoid isomers possible for C_6H_3ClBrI .

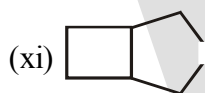
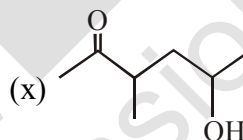
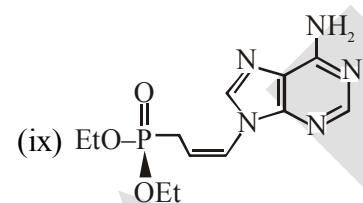
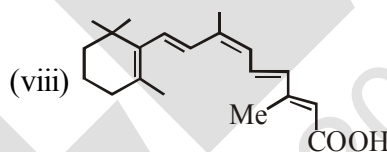
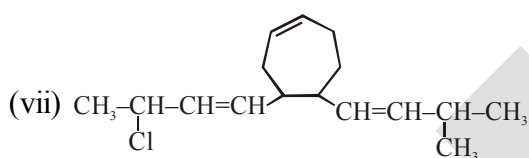
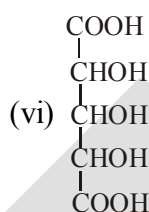
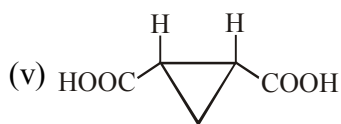
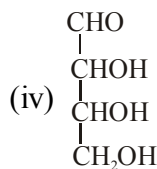
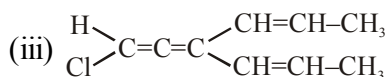
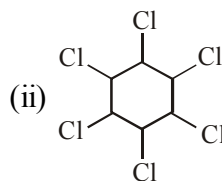
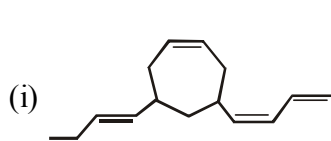
24. What are the relationships between the following pairs of isomers?



Find out total number of structures of X.

26. Calculate the number of chiral center in the molecule Ethyl 2,2-dibromo-4-ethyl-6-methoxy cyclohexane carboxylate.

27. Calculate the total number of stereoisomers possible for



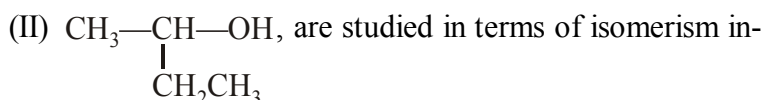
28. How many different chloroethanes are there from the formula $C_2H_{6-n}Cl_n$ (where n can be any integer from 1 to 6)?

EXERCISE # IV (A) (J-MAINS)

1. Racemic mixture is formed by mixing two : **[AIEEE-2002]**

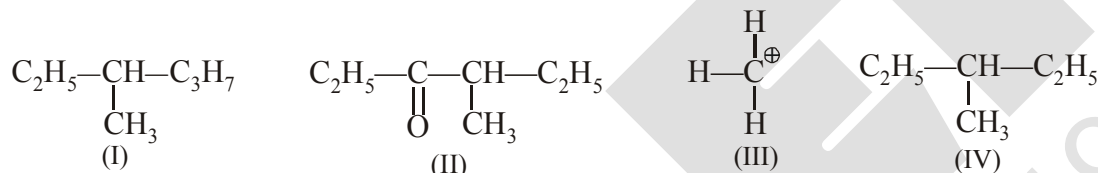
- (1) Isomeric compounds
- (2) Chiral compounds
- (3) Meso compounds
- (4) Enantiomers with chiral carbon

2. Following types of compounds I and II **[AIEEE-2002]**



- (1) Chain isomerism
- (2) Position isomerism
- (3) Conformers
- (4) Stereo isomerism

3. Among the following four structures I to IV



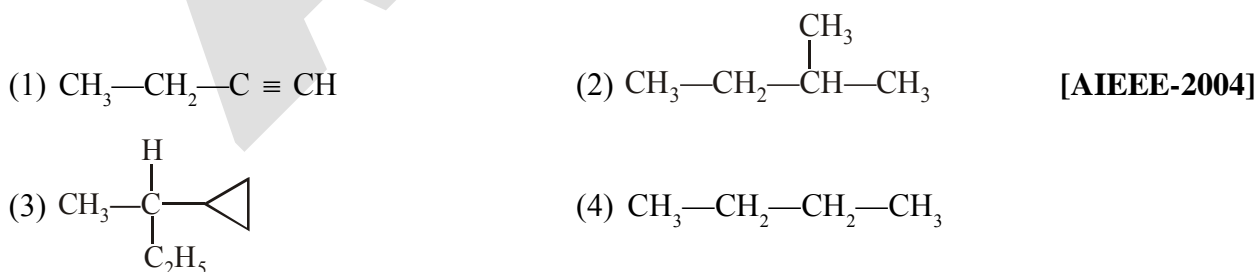
It is true that-

- (1) All four are chiral compounds
- (2) Only I and II are chiral compounds
- (3) Only III is a chiral compound
- (4) Only II and IV are chiral compounds

4. Which of the following will have a meso-isomer also- [AIEEE-2004]

- (1) 2-chlorobutane (2) 2,3-dichlorobutane
(3) 2,3-dichloropentene (4) 2-hydroxy propanoic acid

5. Amongst the following compounds, the optically active alkane having lowest molecular mass is

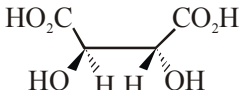


6. Which of following compounds is not chiral [AIEEE-2005]

- (1) 1-chloropentane (2) 2-chloropentane
 (3) 1-chloro-2-methyl pentane (4) 3-chloro-2-methyl pentane

7. Of the five isomeric hexanes, the isomer which can give two monochlorinated compounds is :
 (1) 2-methyl pentane (2) 2,2-dimethyl butane [AIEEE-2005]
 (3) 2,3-dimethyl butane (4) n-hexane

8. Which types of isomerism is shown by 2,3-dichloro butane-
 (1) Structural (2) Geometric (3) Optical (4) Diastereo [AIEEE-2005]

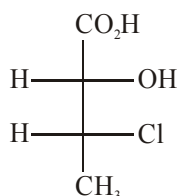
9. The absolute configuration of  is :
 (1) S, S (2) R, R (3) R, S (4) S, R [AIEEE-2008]

10. The number of stereoisomers possible for a compound of the molecular formula $\text{CH}_3\text{--CH=CH--CH(OH)--Me}$ is :-
 (1) 4 (2) 6 (3) 3 (4) 2 [AIEEE-2009]

11. Out of the following, the alkene that exhibits optical isomerism is :-
 (1) 2-methyl-2-pentene
 (2) 3-methyl-2-pentene
 (3) 4-methyl-1-pentene
 (4) 3-methyl-1-pentene [AIEEE-2010]

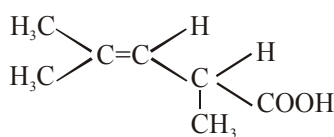
12. The optically inactive compound from the following is :-
 (1) 2-chloropropanal
 (2) 2-chlorobutane
 (3) 2-chloro-2-methylbutane
 (4) 2-chloropentane [JEE-MAIN-2015]

13. The absolute configuration of :
 [JEE-MAIN-2016]



- (1) (2R, 3R) (2) (2R, 3S) (3) (2S, 3R) (4) (2S, 3S)

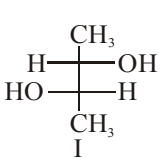
EXERCISE # IV (B) (J-ADVANCE OBJECTIVE)

- The  shows : [IIT-1995]

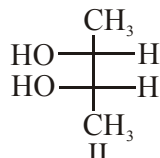
(A) Geometrical isomerism (B) Optical isomerism
(C) Geometrical & optical isomerism (D) tautomerism
- How many optically active stereoisomers are possible for butane -2,3-diol : [IIT-1997]

(A) 1 (B) 2 (C) 3 (D) 4
- The number of possible enantiomeric pairs that can be produced during monochlorination of 2-methyl butane is : [IIT-1997]

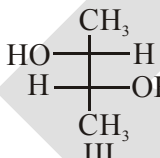
(A) 2 (B) 3 (C) 4 (D) 1
- Identify the pairs of enantiomers and diastereomers from the following compounds I, II and III [IIT-2000]



I



II



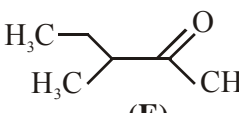
III
- Which of the following compounds exhibits stereoisomerism- [IIT-2002]

(A) 2-Methylbutene-1 (B) 3-Methylbutyne-1
(C) 3-Methylbutanoic acid (D) 2-Methylbutanoic acid
- On monochlorination of 2-methylbutane, the total number of chiral compounds formed is : [IIT-2004]

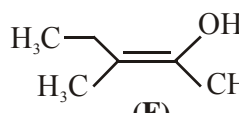
(A) 2 (B) 4 (C) 6 (D) 8
- Statement-I :** Molecules that are not superimposable on their mirror images are chiral
Because

Statement-II : All chiral molecules have chiral centres. [IIT-2007]

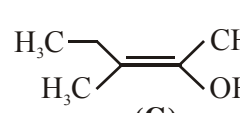
(A) Statement-1 is True, Statement-2 is True ; Statement-2 is a correct explanation for Statement-1
(B) Statement-1 is True, Statement-2 is True ; Statement-2 is NOT a correct explanation for Statement-1
(C) Statement-1 is True, Statement-2 is False.
(D) Statement-1 is False, Statement-2 is True.
- The correct statement(s) concerning the structures E, F and G is (are) [IIT-2008]



(E)



(F)

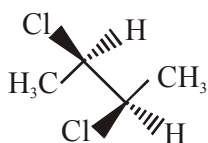


(G)

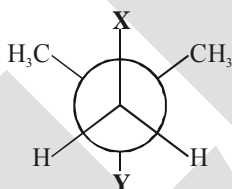
(A) E, F and G are resonance structures (B) E, F and E, G are tautomers
(C) F and G are geometrical isomers (D) F and G are diastereomers

9. The correct statement(s) about the compound given below is (are) :

[IIT-2008]

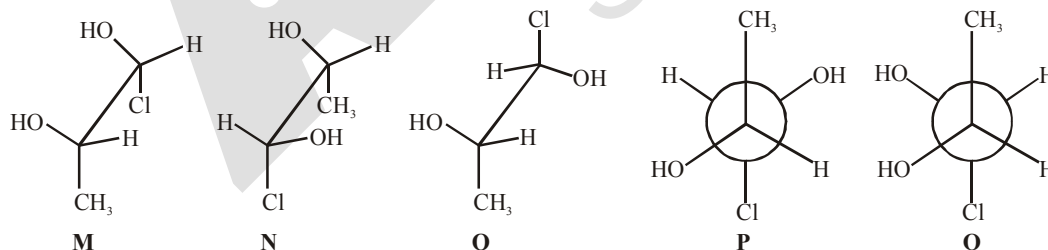


- (A) The compound is optically active
 (B) The compound possesses centre of symmetry
 (C) The compound possesses plane of symmetry
 (D) The compound possesses axis of symmetry
10. The correct statement(s) about the compound $\text{H}_3\text{C}(\text{HO})\text{HC} - \text{CH} = \text{CH} - \text{CH}(\text{OH})\text{CH}_3$ (**X**) is (are) : [IIT-2009]
- (A) The total number of stereoisomers possible for **X** is 6
 (B) The total number of diastereomers possible for **X** is 3
 (C) If the stereochemistry about the double bond in **X** is trans, the number of enantiomers possible for **X** is 4
 (D) If the stereochemistry about the double bond in **X** is cis, the number of enantiomers possible for **X** is 2
11. In the Newman projection for 2,2-dimethylbutane [IIT-2010]



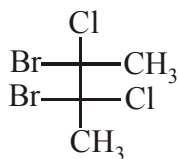
X and **Y** can respectively be –

- (A) H and H (B) H and C_2H_5 (C) C_2H_5 and H (D) CH_3 and CH_3
12. Which of the given statement(s) about **N**, **O**, **P** and **Q** with respect to **M** is (are) correct ? [JEE-2012]

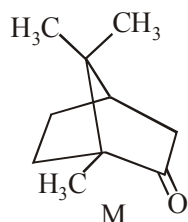


- (A) **M** and **N** are non-mirror image stereoisomers
 (B) **M** and **O** are identical
 (C) **M** and **P** are enantiomers
 (D) **M** and **Q** are identical

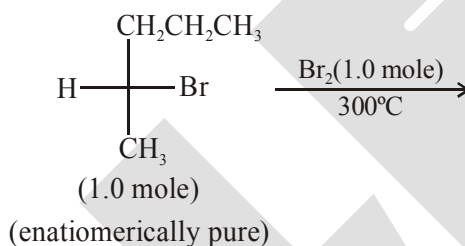
13. The total number(s) of stable conformers with **non-zero** dipole moment for the following compound is (are) [JEE-2014]



14. The total number of stereoisomers that can exist for M is : [JEE-2015]

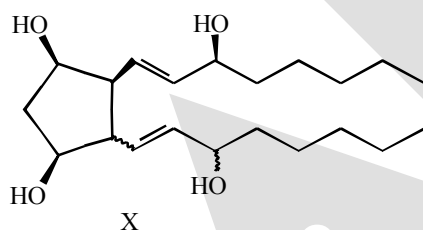


15. In the following monobromination reaction, the number of possible chiral products is : [JEE-2016]



16. For the given compound X, the total number of optically active stereoisomers is ____.

[IIT-JEE 2018]



— This type of bond indicates that the configuration at the specific carbon and the geometry of the double bond is fixed

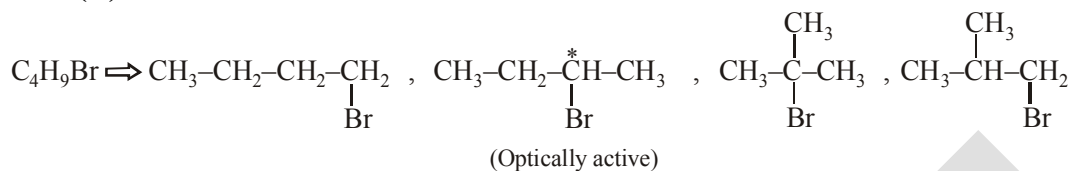
~~~~ This type of bond indicates that the configuration at the specific carbon and the geometry of the double bond is NOT fixed



## ANSWER-KEY

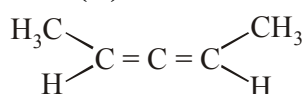
## EXERCISE # I (MAINS ORIENTED)

- |           |                 |           |                 |           |                 |           |                 |
|-----------|-----------------|-----------|-----------------|-----------|-----------------|-----------|-----------------|
| <b>1.</b> | <b>Ans. (C)</b> | <b>2.</b> | <b>Ans. (C)</b> | <b>3.</b> | <b>Ans. (D)</b> | <b>4.</b> | <b>Ans. (D)</b> |
| <b>5.</b> | <b>Ans. (A)</b> | <b>6.</b> | <b>Ans. (A)</b> | <b>7.</b> | <b>Ans. (A)</b> | <b>8.</b> | <b>Ans. (D)</b> |
| <b>9.</b> | <b>Ans. (B)</b> |           |                 |           |                 |           |                 |



Optically active isomers  $\Rightarrow 2$

10. Ans. (B)                      11. Ans. (D)                      12. Ans. (A)  
13. Ans. (C)



- 14. Ans. (B)**                      **15. Ans. (C)**                      **16. Ans. (D)**

- 17. Ans. (C)**

- 18. Ans. (A)**

$\text{Cl}-\text{CH}=\text{C}=\text{C}=\text{CH}-\text{Cl}$  is a planar structure

- 19. Ans. (A)**

- 20. Ans. (C)**

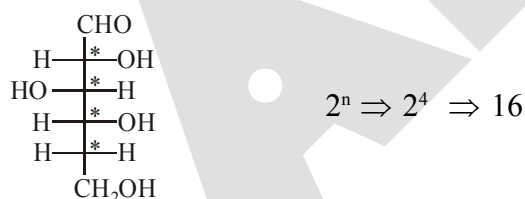
Meso tartaric acid and d-tartaric acid are not mirror images of each other so they are diastereomers.

- 21. Ans. (A)**



- 22. Ans. (C)**                      **23. Ans. (D)**                      **24. Ans. (B)**

- 25. Ans. (C)**

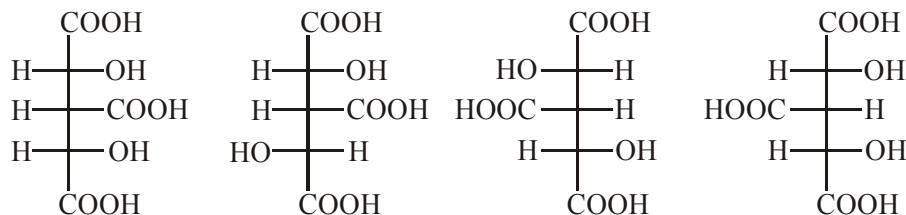


- 26. Ans. (B)** **27. Ans. (B)**

- 28. Ans. (B)**

Optically active compounds are resolvable.

- 29. Ans. (B)**

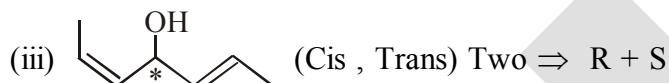
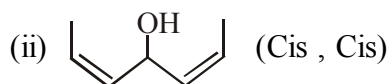
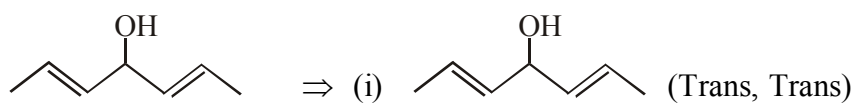




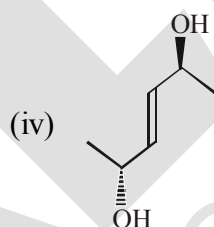
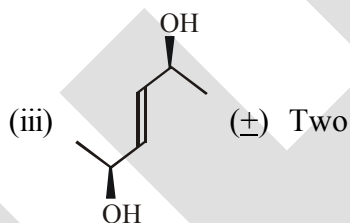
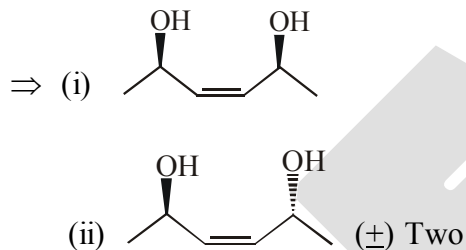
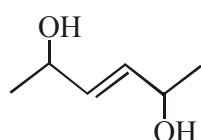
2. Ans. (C)

3. Ans. (B)

4. Ans. (A)



Total isomers = 4



Total = 6 isomer

5. Ans. (A,C,D)

6. Ans. (A,C)

Optically active compounds are resolvable and A &amp; C are optically inactive

7. Ans. (B,C,D)

8. Ans. (A,B,C)

9. Ans. (A,B,D)

10. Ans. (C,D)

11. Ans. (A,D)

12. Ans. (A,C)

13. Ans. (A,B,C,D)

14. Ans. (C)

15. Ans. (D)

16. Ans. (C)

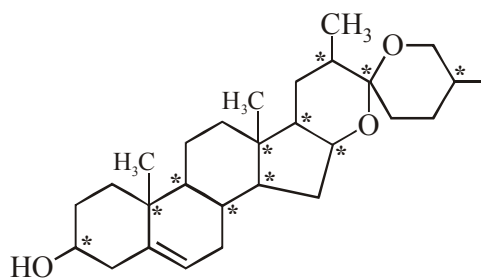
17. Ans. (D)

18. Ans. (A)  $\rightarrow$  P ; (B)  $\rightarrow$  R ; (C)  $\rightarrow$  Q ; (D)  $\rightarrow$  R

19. Ans. (1-R, 2-P, 3-Q, 4-S)

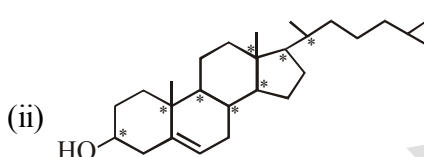
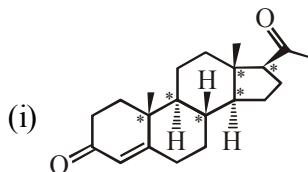
20. Ans. (1-S, 2-R, 3-Q, 4-Q)

**21. Ans. (11)**

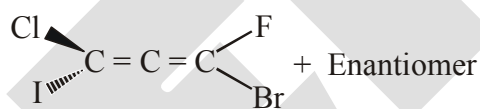
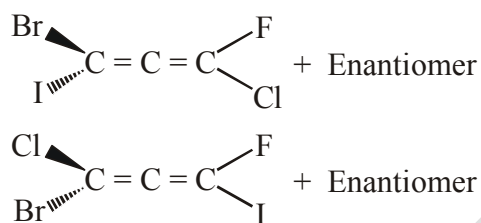


**22. Ans. (i) 6, (ii) 8**

### Explanation

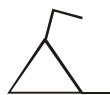


**23. Ans. (6)**



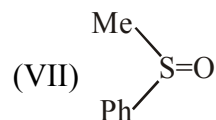
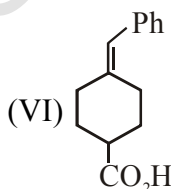
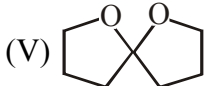
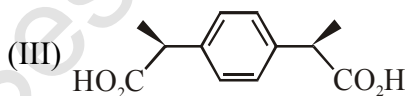
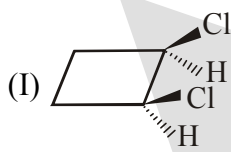
**24. Ans. (A,B)**

**25. Ans. (8)**



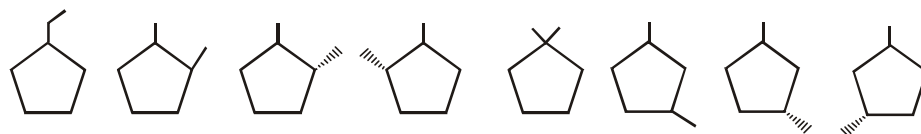
4 Optically Active Isomers    2 Optically Active    2 Optically Active  
 $2 + 2 + 4 = 8$

**26. Ans. (6)**

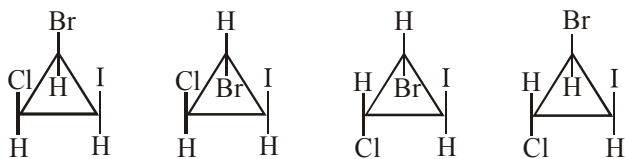


**27. Ans.** Achiral : I, III , IV ; chiral : II,V, VI, VII

**28. Ans. (8)**



29. Ans. (4)



30. Ans. (8)



Stereogenic centre = 3

total number of stereoisomer =  $2^3 = 8$ 

31. Ans. (3)

32. Ans. (C)

**EXERCISE#III (JEE-ADVANCE ORIENTED LEVEL # II)****Single Correct Type :**

1. Ans. (A)

2. Ans. (D)

3. Ans. (8)

4. Ans. (i) (B) ; (ii) (C)

5. Ans. (C)

6. Ans. (C)

**Multiple Correct Type :**

7. Ans. (A,C)

8. Ans. (A,C,D)

9. Ans. (C)

10. Ans. (C)

11. Ans. (B)

12. Ans. (A,D)

**Comprehension Type :**

13. Ans. (B)

14. Ans. (C)

15. Ans. (D)

M.W. of MSG = 169

$$C = \frac{169 \text{ gm}}{845 \text{ ml}}$$

$$\ell = 200 \text{ mm} = 2 \text{ dm}$$

$$\alpha_{\text{obs}} = +9.6^\circ$$

$$[\alpha]_{\text{sp}} = \frac{\alpha_{\text{obs}}}{C \cdot \ell} = \frac{9.6}{\frac{169}{845} \times 2} = -24^\circ$$

16. Ans. (C)

$$ee = \frac{[\alpha]_{\text{mixture}}}{[\alpha]_{\text{pure}}} \times 100 = \frac{-20^\circ}{-24^\circ} \times 100 = 83.3\%$$

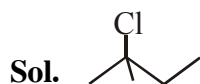
$$\therefore \text{RM} = 100 - 83.3 \Rightarrow 16.7\% \begin{cases} \rightarrow d = 8.35 \\ \rightarrow l = 8.35 \end{cases}$$

$$\begin{aligned} \text{Total } (-) \text{ MSG} &= 83.3 + 8.35 \\ &= 91.6\% \end{aligned}$$



## EXERCISE # IV (A) (J-MAINS)

- |              |              |              |             |
|--------------|--------------|--------------|-------------|
| 1. Ans. (4)  | 2. Ans. (4)  | 3. Ans. (2)  | 4. Ans. (2) |
| 5. Ans. (3)  | 6. Ans. (1)  | 7. Ans. (3)  | 8. Ans. (3) |
| 9. Ans. (2)  | 10. Ans. (1) | 11. Ans. (4) |             |
| 12. Ans. (3) |              |              |             |

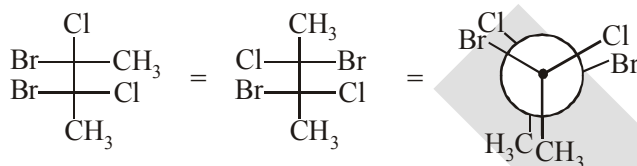


It achiral \ optically inactive

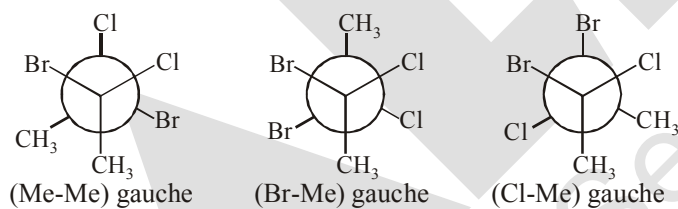
13. Ans. (3)

## EXERCISE # IV (B) (J-ADVANCE OBJECTIVE)

- |                                                                       |                  |                |
|-----------------------------------------------------------------------|------------------|----------------|
| 1. Ans. (B)                                                           | 2. Ans. (B)      | 3. Ans. (A)    |
| 4. Ans. Enantiomers - I and III ; Diastereomers - I & II and II & III |                  |                |
| 5. Ans. (D)                                                           | 6. Ans. (B)      | 7. Ans. (C)    |
| 8. Ans. (B,C,D)                                                       | 9. Ans. (A,D)    | 10. Ans. (A,D) |
| 11. Ans. (B,D)                                                        | 12. Ans. (A,B,C) |                |
| 13. Ans. (3)                                                          |                  |                |

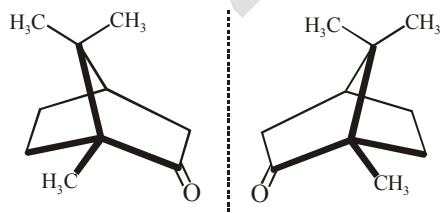


Stable conformer (with  $\mu \neq 0$ )



14. Ans. (2)

Sol. M is a organic compound known as camphor. M contains two **rigid** chiral centre so it can exist only in **two** enantiomeric forms.



15. Ans. (5)      16. Ans. (7)

**SOLID STATE**

ALLERK  
Session 2019-20



## SOLID STATE

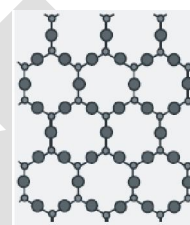
### 1. THE SOLID STATE :

The solids are characterised by incompressibility, rigidity and mechanical strength. The molecules, atoms or ions in solids are closely packed i.e. they are held together by strong forces and can not move about at random. Thus solids have definite volume, shape, slow diffusion, low vapour pressure and possess the unique property of being rigid.

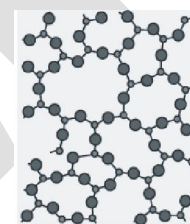
### 2. AMORPHOUS AND CRYSTALLINE SOLIDS

Solids can be classified as *crystalline* or *amorphous* on the basis of the nature of order present in the arrangement of their constituent particles. A crystalline solid usually consists of a large number of small crystals, each of them having a definite characteristic geometrical shape. In a crystal, the arrangement of constituent particles (atoms, molecules or ions) is ordered. It has **long range order** which means that there is a regular pattern of arrangement of particles which repeats itself periodically over the entire crystal. Sodium chloride and quartz are typical examples of crystalline solids. An amorphous solid (Greek *amorphos* = no form) consists of particles of irregular shape. The arrangement of constituent particles (atoms, molecules or ions) in such a solid has only **short range order**. In such an arrangement, a regular and periodically repeating pattern is observed over short distances only.

Such portions are scattered and in between, the arrangement is disordered. The structures of quartz (crystalline) and quartz glass (amorphous) are shown in Fig. 1.1 (a) and (b) respectively. While the two structures are almost identical, yet in the case of amorphous quartz glass there is no **long range order**. The structure of amorphous solids is similar to that of liquids. Glass, rubber and plastics are typical examples of amorphous solids. Due to the differences in the arrangement of the constituent particles, the two types of solids differ in their properties.



(a)



(b)

Fig. 1.1 : Two dimensional structure of (a) quartz and (b) quartz glass

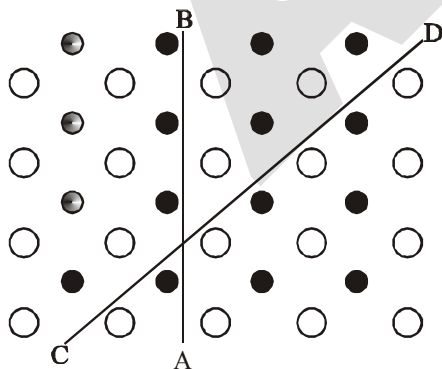


Fig. 1.2 : Anisotropy in crystals is due to different arrangement of particles along different directions.

Crystalline solids have a sharp melting point. On the other hand, amorphous solids soften over a range of temperature and can be moulded and blown into various shapes. On heating they may become crystalline at some temperature. Some glass objects from ancient civilisations are found to become milky in appearance because of some crystallisation. Like liquids, amorphous solids have a tendency to flow, though very slowly. Therefore, sometimes these are called **pseudo solids** or **super cooled liquids**. Glass panes fixed to windows or doors of old buildings are invariably found to be slightly thicker at the bottom than at the top. This is because the glass flows down very slowly and makes the bottom portion slightly thicker.

Crystalline solids are **anisotropic** in nature, that is, some of their physical properties like electrical resistance or refractive index show different values when measured along different directions in the same crystals. This arises from different arrangement of particles in different directions. This is illustrated in Fig. 1.2. Since the arrangement of particles is different along different directions, the value of same physical property is found to be different along each direction. Amorphous solids on the other hand are **isotropic** in nature. It is because there is no *long range* order in them and arrangement is irregular along all the directions. Therefore, value of any physical property would be same along any direction. These differences are summarised in Table below :

**Distinction between Crystalline and Amorphous Solids**

| Property                                      | Crystalline Solids                                                                                                 | Amorphous Solids                                                                   |
|-----------------------------------------------|--------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------|
| Shape                                         | Definite characteristic geometrical shape                                                                          | Irregular shape                                                                    |
| Melting point                                 | Melt at a sharp and characteristic temperature                                                                     | Gradually soften over a range of temperature                                       |
| Cleavage property                             | When cut with a sharp edged tool, they split into two pieces and the newly generated surfaces are plane and smooth | When cut with a sharp edged tool, they cut into two pieces with irregular surfaces |
| Heat of fusion                                | They have a definite and characteristic heat of fusion                                                             | They do not have definite heat of fusion                                           |
| Anisotropy                                    | Anisotropic in nature                                                                                              | Isotropic in nature                                                                |
| Nature                                        | True solids                                                                                                        | Pseudo solids or super cooled liquids                                              |
| Order in arrangement of constituent particles | Long range order                                                                                                   | Only short range order.                                                            |

**Ex.1** Classify the following as amorphous or crystalline solids :

- |                        |                 |
|------------------------|-----------------|
| (a) Polyurethane       | (b) Napthalene  |
| (c) Benzoic acid       | (d) Teflon      |
| (e) Potassium nitrate  | (f) Cellophane  |
| (g) Polyvinyl chloride | (h) Fibre glass |
| (i) Copper             |                 |

**Sol.** Crystalline : (b) , (c) , (e) , (i)

Amorphous : (a) , (d) , (f) , (g), (h)

**Note :** Polymeric substances are generally amorphous.

**Ex.2** Classify the following solids in different categories based on the nature of intermolecular forces operating in them :

- Sol.** Ionic solids : (a), (g)

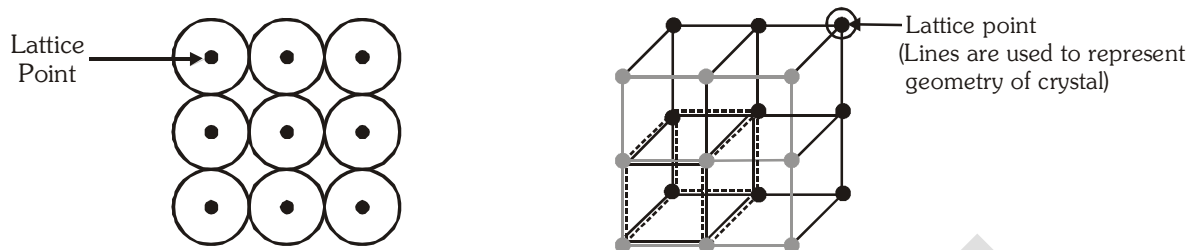
**Metallic solids :** (b), (i), (l)

Molecular solids : (c), (d), (e), (f), (j)

Covalent network solids.: (h), (k)

## 4.0 SOME BASIC DEFINITION :

## 4.1 SPACE LATTICE (CRYSTAL LATTICE :



The main characteristic of crystalline solids is a regular and repeating pattern of constituent particles. If the three dimensional arrangement of constituent particles in a crystal is represented diagrammatically, in which each particle is depicted as a point, the arrangement is called crystal lattice. Thus, **a regular three dimensional arrangement of points in space is called a crystal lattice**. A portion of a crystal lattice is shown in Fig. The following are the characteristics of a crystal lattice:

- Each point in a lattice is called **lattice point** or **lattice site**.
- Each point in a crystal lattice represents one constituent particle which may be an atom, a molecule (group of atoms) or an ion.
- Lattice points are joined by straight lines to bring out the geometry of the lattice.

## 4.2. UNIT CELL :

Unit cell is the smallest portion of a crystal lattice which, when repeated in different directions, generates the entire lattice.

A unit cell is characterized by the edge lengths  $a$ ,  $b$  and  $c$  along the three edges of the unit cell and the angles  $\alpha$ ,  $\beta$  and  $\gamma$  between the pair of edges :  $bc$ ,  $ca$  and  $ab$ , respectively.

## TYPE OF UNIT CELLS -

## 4.2.1 Primitive and Centred Unit cells

Unit cells can be broadly divided into two categories, primitive and centred unit cells.

## (a) Primitive Unit Cells (P)

When constituent particles are present only on the corner positions of a unit cell, it is called as **primitive unit cell**.

## (b) Centred Unit Cells

When a unit cell contains one or more constituent particles present at positions other than corners in addition to those at corners, it is called a centred unit cell. **Centred unit cells** are of three types:

- Body-Centred Unit Cells (I) :** Such a unit cell contains one constituent particle (atom, molecule or ion) at its body-centre besides the ones that are at its corners.
- Face-Centred Unit Cells (F) :** Such a unit cell contains one constituent particle present at the centre of each face, besides the ones that are at its corners.
- End-Centred Unit Cells (E) :** In such a unit cell, one constituent particle is present at the centre of any two opposite faces besides the ones present at its corners.

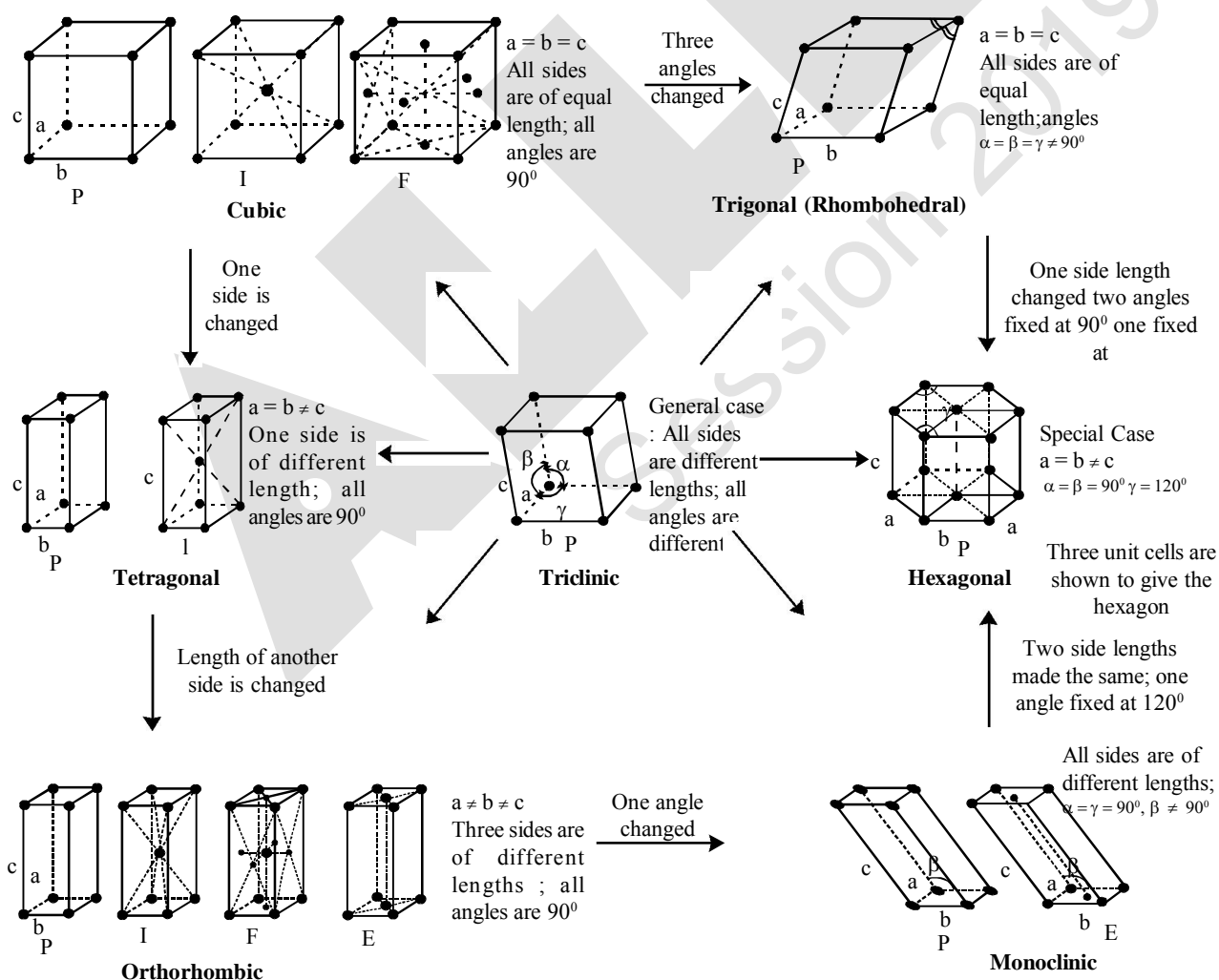
### 4.3. THE SEVEN CRYSTAL SYSTEMS

On the basis of the classification of symmetry, the lattice have been divided into seven systems. These can be grouped into 7 crystal systems. These seven systems with the characteristics of their axes (angles and intercepts) along with some examples of each are given in the following table :

Seven Primitive Unit cells and their Possible Variations as Centred Unit Cells

| Crystal system           | Possible Variations                                | Axial distance or edge lengths | Axial angles                                      | Examples                                                                                                |
|--------------------------|----------------------------------------------------|--------------------------------|---------------------------------------------------|---------------------------------------------------------------------------------------------------------|
| Cubic                    | Primitive, body-centred, Face centre               | $a = b = c$                    | $\alpha = \beta = \gamma = 90^\circ$              | NaCl, Zinc blende, Cu                                                                                   |
| Tetragonal               | Primitive, Body-centred                            | $a = b \neq c$                 | $\alpha = \beta = \gamma = 90^\circ$              | White tin, $\text{SnO}_2$ , $\text{TiO}_2$ , $\text{CaSO}_4$                                            |
| Orthorhombic             | Primitive, Body-centred, Face-centred, End-centred | $a \neq b \neq c$              | $\alpha = \beta = \gamma = 90^\circ$              | Rhombic sulphur, $\text{KNO}_3$ , $\text{BaSO}_4$                                                       |
| Hexagonal                | Primitive                                          | $a = b \neq c$                 | $\alpha = \beta = 90^\circ, \gamma = 120^\circ$   | Graphite, ZnO, CdS,                                                                                     |
| Rhombohedral or Trigonal | Primitive                                          | $a = b = c$                    | $\alpha = \beta = \gamma \neq 90^\circ$           | Calcite ( $\text{CaCO}_3$ ), HgS (Cinnabar)                                                             |
| Monoclinic               | Primitive, End-centred                             | $a \neq b \neq c$              | $\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$ | Monoclinic sulphur, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$                                 |
| Triclinic                | Primitive                                          | $a \neq b \neq c$              | $\alpha \neq \beta \neq \gamma \neq 90^\circ$     | $\text{K}_2\text{Cr}_2\text{O}_7$ , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , $\text{H}_3\text{BO}_3$ |

### 4.4. BRAVAIS LATTICES : There are 14 Bravais lattices :



**4.5. CO-ORDINATION NUMBER :**

The number of nearest particles around a specific particle in a given crystalline substance is called *co-ordination* number.

**4.6. PACKING EFFICIENCY OR PACKING DENSITY (P.E.) :**

Packing efficiency is defined as the ratio of volume occupied by the constituent particles to the total volume of the crystalline substance.

$$\text{P.E.} = \frac{\text{Volume occupied by particles present in a crystal}}{\text{Volume of crystal}}$$

$$\text{P.E.} = \frac{\text{Volume occupied by particles present in unit cell}}{\text{Volume of Unit Cell}}$$

$$\text{P.E.} = \frac{Z \times (4/3)\pi r^3}{V}, \text{ where } Z = \text{number of atoms present in unit cell}$$

**4.7. DENSITY OF THE CRYSTAL :**

$$\text{Density of crystal} = \text{Density of an unit cell} = \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}}$$

$$\text{Mass of the unit cell} = \text{Number of particles present in a unit cell} \times \text{Mass of one particles} = Z \times m$$

$$\text{But mass of one particles (m)} = \frac{\text{Particle mass}}{\text{Avogadro Number}} = \frac{M}{N_A}$$

$$\text{Mass of an unit cell} = Z \times \frac{M}{N_A}$$

$$\text{Density of an unit cell} = \frac{Z \times \frac{M}{N_A}}{V}$$

$$\therefore \text{Density of Crystal, } d = \text{Density of an unit cell} = \frac{Z \times M}{V \times N_A} \text{ g cm}^{-3}$$

**5.0 ANALYSIS OF CUBIC CRYSTAL :****5.1. GEOMETRY OF A CUBE**

Number of corners = 8

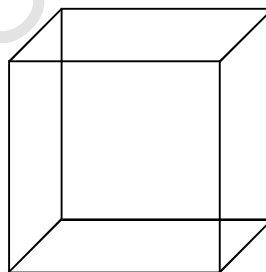
Number of faces = 6

Number of edges = 12

Number of cube centre = 1

Number of cube diagonals = 4

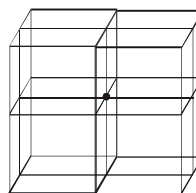
Number of face diagonals = 12



## 5.2 CONTRIBUTION OF A CONSTITUENT PARTICLE AT DIFFERENT SITES OF CUBE :

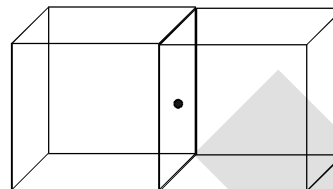
### 5.2.1 A corner of a cube is common in 8 cubes.

So  $\frac{1}{8}$  th part of a particle is present at this corner of cube.



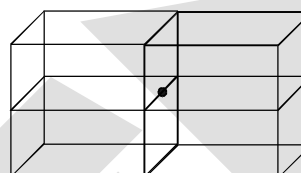
### 5.2.2 A face of a cube is common in 2 cubes.

So  $\frac{1}{2}$  th part of a particle is present at the face of a cube.



### 5.2.3 An edge of a cube is common in four cubes,

so  $\frac{1}{4}$  th part of particle is present at the edge of a cube

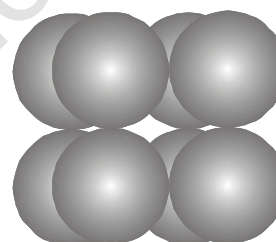
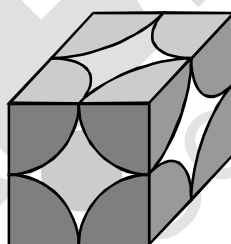
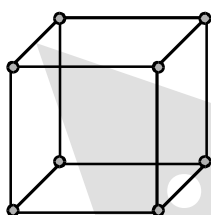


## 5.3 TYPE OF CUBIC UNIT CELL :

### 5.3.1 Simple/Primitive/Basic Unit cell (Simple cubic, SC) ;

A unit cell having lattice point only at corners called as primitive or simple unit cell. In this case there is one particle at each of the eight corners of the unit cell.

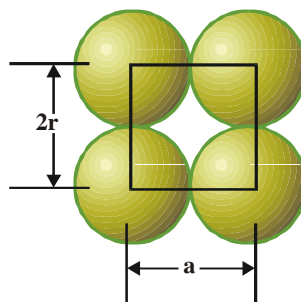
Considering a particles at one corner as the centre, it will be found that this atom is surrounded by six equidistant neighbours (particles) and thus the co-ordination number will be six. If 'a' is the side of the unit cell, then the distance between the nearest neighbours shall be equal to 'a'.



### (a) Relationship between Edge length 'a' and Particle radius 'r' :-

$$a = 2r$$

i.e.,  $r = \frac{a}{2}$



(One face of SC)



(b) **Number of particles present in unit cell (Z) :** In this case one particle lies at each corner.

Hence simple cubic unit cell contains a total of  $\frac{1}{8} \times 8 = 1$  particle /unit cell.

(c) **Packing efficiency (P. E.) :**

$$\text{P.E.} = \frac{\text{Volume occupied by particles present in unit cell}}{\text{Volume of unit cell}} = \frac{Z \times \frac{4}{3} \pi r^3}{V} \quad \left[ \text{Volume of atom} = \frac{4}{3} \pi r^3 \right]$$

$$\text{P.E.} = \frac{1 \times \frac{4}{3} \times \pi \times \left(\frac{a}{2}\right)^3}{a^3} = \frac{\pi}{6} = 0.52 \text{ or } 52\% \quad \left[ r = \frac{a}{2} \text{ and } V = a^3, Z = 1 \right]$$

In SC, 52% of total volume is occupied by particles.

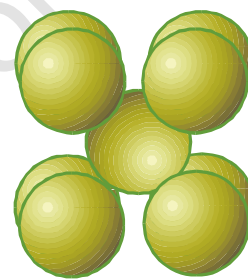
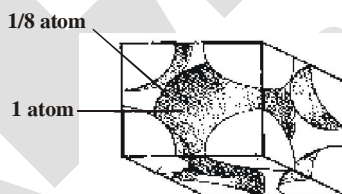
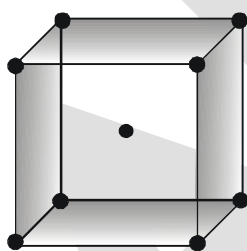
$\therefore$  Void space  $\approx (100 - 52) = 48\%$

(d) **Coordination number (CN)**

| Nearest neighbour | Distance    | Number |
|-------------------|-------------|--------|
| 1                 | a           | 6      |
| 2                 | $\sqrt{2}a$ | 12     |
| 3                 | $\sqrt{3}a$ | 8      |

### 5.3.2. Body Centred Cubic unit cell (BCC):

A unit cell having lattice point at the body centre in addition to the lattice points at every corner is called as body centered unit cell. Here the central particle is surrounded by eight equidistant particles and hence the co-ordination number is eight. The nearest distance between two particles will be  $\frac{a\sqrt{3}}{2}$

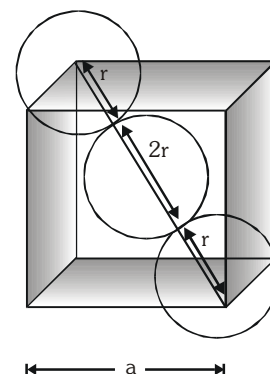


(a) **Relationship between edge length 'a' and particle radius 'r' :**

In BCC, along cube diagonal all particles touches each other and the length of cube diagonal is  $\sqrt{3}a$ .

So,  $\sqrt{3}a = 4r$

i.e.  $r = \frac{\sqrt{3}a}{4}$





(b) Number of particle present in unit cell (Z):

$$Z = \left( \frac{1}{8} \times 8 \right) + (1 \times 1) = 1 + 1 = 2 \text{ particles/unit cell.}$$

(Corner) (Body centre)

In this case one particle lies at the each corner of the cube. Thus contribution of the 8 corners is  $\left( \frac{1}{8} \times 8 \right) = 1$ , while that of the body centred is 1 in the unit cell. Hence total number of particles per unit cell is  $1 + 1 = 2$

(c) Packing efficiency :

$$\text{P.E.} = \frac{Z \times \frac{4}{3} \pi r^3}{V} = \frac{2 \times \frac{4}{3} \times \pi \left( \frac{\sqrt{3}a}{4} \right)^3}{a^3} = \frac{\sqrt{3}\pi}{8} = 0.68 \text{ or } 68\% \quad [Z = 2, r = \frac{\sqrt{3}a}{4}, V = a^3]$$

In BCC, 68% of total volume is occupied by particles.

$$\therefore \text{Void space} = 100 - 68 = 32 \%$$

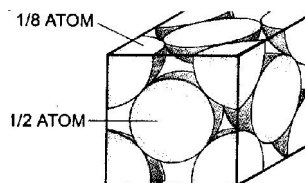
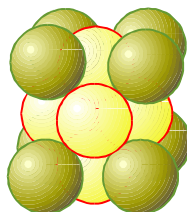
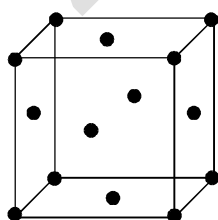
(d) Coordination number (CN)

| Nearest neighbour | Distance               | Number |
|-------------------|------------------------|--------|
| 1                 | $\sqrt{3} \frac{a}{2}$ | 8      |
| 2                 | a                      | 6      |
| 3                 | $\sqrt{2} a$           | 12     |

5.3.3 Face Centred Cubic unit cell (FCC):

A unit cell having lattice point at every face centre in addition to the lattice point at every corner called as face centred unit cell.

In this case there are eight particles at the eight corners of the unit cell and six particles at the centre of six faces. Considering a particle at the face centre as origin, it will be found that this face is common to two cubes and there are twelve points surrounding it situated at a distance which is equal to half the face diagonal of the unit cell. Thus the co-ordination number will be twelve and the distance between the two nearest particles will be  $\frac{a}{\sqrt{2}}$ .

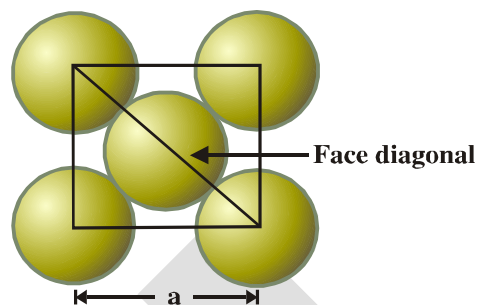


**(a) Relationship between edge length 'a' and atomic radius 'r' :**

In FCC, along the face diagonal all atoms touches each other and the length of face diagonal is  $\sqrt{2}a$ .

So  $4r = \sqrt{2}a$

i.e.  $r = \frac{a}{2\sqrt{2}}$

**(b) Number of particles per unit cell : (Z)**

$$Z = \left( \frac{1}{8} \times 8 \right) + \left( 6 \times \frac{1}{2} \right) = 1 + 3 = 4 \text{ particles/unit cell}$$

Corner      faces

In this case, one particle lies at the each corner of the cube and one particle lies at the centre of each face of the cube. It may noted that only  $1/2$  of each face sphere lie within the unit cell and there are six such faces. The total contribution of 8 corners is  $\left( \frac{1}{8} \times 8 \right) = 1$ , while that of 6 face centred particles is  $\left( \frac{1}{2} \times 6 \right) = 3$  in the unit cell.

Hence, total number of particles per unit cell is  $1 + 3 = 4$

**(c) Packing efficiency :**

$$\text{P.E.} = \frac{Z \times \frac{4}{3} \pi r^3}{V} \quad [Z = 4, r = \frac{a}{2\sqrt{2}}, V = a^3]$$

$$= \frac{4 \times \frac{4}{3} \pi \times \left( \frac{a}{2\sqrt{2}} \right)^3}{a^3} = \frac{\pi}{3\sqrt{2}} = 0.74 \text{ or } 74\%$$

In FCC, 74% of total volume is occupied by particles. This is maximum for crystals having identical particles.

$\therefore$  Void space =  $100 - 74 = 26\%$

**(d) Coordination number (CN)**

| Nearest neighbour | Distance              | Number |
|-------------------|-----------------------|--------|
| 1                 | $\frac{a}{\sqrt{2}}$  | 12     |
| 2                 | $a$                   | 6      |
| 3                 | $\frac{\sqrt{3}}{2}a$ | 24     |

### 5.4 SUMMARY OF CUBIC CRYSTAL :

| Unit cell              | No. of particles per unit cell (Z) | 2r =                  | CN | Volume occupied by particles (%) |
|------------------------|------------------------------------|-----------------------|----|----------------------------------|
| Simple cube(SC)        | 1                                  | a                     | 6  | 52                               |
| Body centred cube(BCC) | 2                                  | $\frac{a\sqrt{3}}{2}$ | 8  | 68                               |
| Face centred cube(FCC) | 4                                  | $\frac{a}{\sqrt{2}}$  | 12 | 74                               |

**Ex.3.** An element (atomic mass = 60) having face centred cubic crystal has a density of  $6.23 \text{ g cm}^{-3}$ .

What is the edge length of the unit cell ? (Avogadro constant,  $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$ )

**Sol.** Since element has fcc structure hence there are 4 atoms in a unit cell ( $Z = 4$ ), Atomic mass is 60 ( $M = 60$ ),  $N_A = 6.02 \times 10^{23}$  and  $d = 6.23 \text{ g cm}^{-3}$ .

$$\therefore d = \frac{Z \times M}{V \times N_A}$$

$$\text{or } V = \frac{Z \times M}{d \times N_A} = \frac{(4) (60 \text{ g mol}^{-1})}{(6.23 \text{ g cm}^{-3})(6.02 \times 10^{23} \text{ mol}^{-1})}$$

$$= 64 \times 10^{-24} \text{ cm}^3$$

Let  $\ell$  be the length of the edge of the unit cell.

$$\therefore \ell^3 = V = 64 \times 10^{-24} \text{ cm}^3 \quad \text{or} \quad \ell = 4.0 \times 10^{-8} \text{ cm}$$

**Ex.4.** The density of Al is  $5.4 \text{ g/cm}^3$ . If it crystallise in fcc lattice, determine its atomic radius.

$$\text{Sol. } d = \frac{ZM}{N_A \cdot V} \Rightarrow 5.4 = \frac{4 \times 27}{N_A \times (2\sqrt{2}r)^3}$$

$$\therefore r = 1.136 \times 10^{-8} \text{ cm} = 1.136 \text{ \AA}$$

**Ex.5.** A solid crystallises in cubic crystal in which 'X' atoms occupy all the corners and body centres and 'Y' atoms occupy all the face-centres. What is the simplest formula of solid?

$$\text{Sol. } Z_X = 8 \times \frac{1}{8} + 1 = 2$$

$$Z_Y = 6 \times \frac{1}{2} = 3$$

$$\therefore \text{Simplest formula of solid} = X_2Y_3$$

## 6. CLOSE PACKING OF IDENTICAL SOLID SPHERES

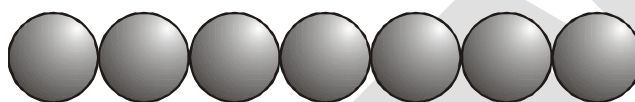
The solids which have non-directional bonding, their structures are determined on the basis of geometrical consideration. For such solids, it is found that the lowest energy structure is that in which each particle is surrounded by the greatest possible number of neighbours. In order to understand the structure of such solids, let us consider the particles as hard sphere of equal size in three directions. Although there are many ways to arrange the hard spheres but the one in which maximum available space is occupied will be economical which is known as **closed packing**.

To clearly understand the packing of these spheres, the packing can be categorised as :

- (i) Close packing in one dimension.
- (ii) Close packing in two dimension.
- (iii) Close packing in three dimension.

### 6.1 CLOSE PACKING IN ONE DIMENSION :

In one dimension , only one arrangement of spheres is possible as shown in fig.



Close packing of spheres in one dimension

Each sphere is touched by other two spheres, hence coordination numbers of packing is two.

### 6.2 CLOSE PACKING IN TWO DIMENSION :

Two possible types of two dimensional packing are

- (i) Square close packing in two dimension.
- (ii) Hexagonal close packing in two dimension.

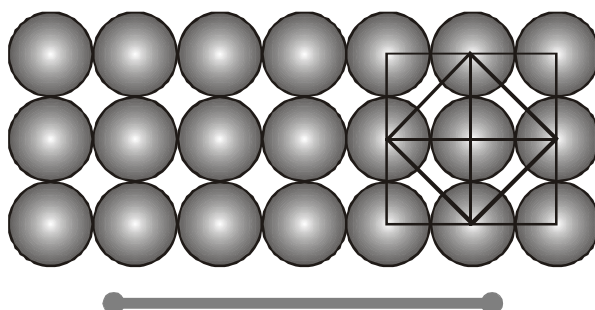
#### (i) Square close packing in two dimension :

When two rows are placed in such a manner, that spheres of one row are placed immediately below of the other, the resulting packing is called two dimensional square close packing.

- (i) Since all the rows are identical, the packing is called AAA ..... type packing.
- (ii) Each sphere is touched by four other, hence coordination number is four.
- (iii) If centres of spheres are connected, square cells are formed , hence it also called two dimensional square packing.
- (iv) This type of packing is not very effective in terms of utilisation of space.

$$(v) \text{ Packing efficiency in 2-D} = \frac{1 \times \pi r^2}{a^2} = \frac{1 \times \pi (a/2)^2}{a^2} = \frac{\pi}{4} = 0.78 \text{ or } 78\%$$

$$(vi) \text{ Packing efficiency in 3-D} = \frac{1 \times \frac{4}{3} \pi \left(\frac{a}{2}\right)^3}{a^3} = 0.52 \text{ or } 52\% \text{ [In 3-D, its unit cell is simple cubic]}$$



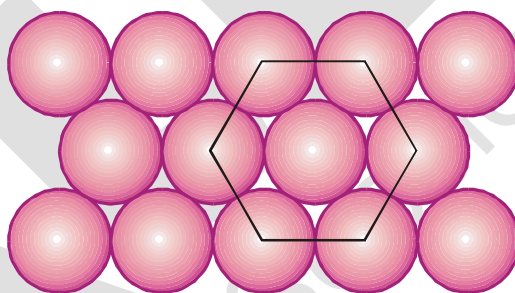
**(ii) Hexagonal close packing in two dimension :**

If various one dimensional close pack rows are placed in such a way that spheres of top row fits in depression of bottom row spheres, the resulting packing is called two dimensional hexagonal close packing.

- (i) Every third row sphere comes exactly at top of first row sphere, hence the packing is called ABABAB ..... packing.
- (ii) If centres are joined, hexagonal unit cells are formed. Hence this is called two dimensional hexagonal close packing.
- (iii) This packing is most efficient in utilising space in two dimensional arrangement.
- (iv) Each sphere is touched by six other, hence coordination number is six.

(v) Packing efficiency in 2-D =  $\frac{3 \times \pi \left(\frac{a}{2}\right)^2}{\frac{a^2 \sqrt{3}}{4} \times 6} = \frac{\pi}{2\sqrt{3}} = 0.90$  or 90%

(vi) Packing efficiency in 3-D =  $\frac{3 \times \frac{4}{3} \pi \left(\frac{a}{2}\right)^3}{\frac{a^2 \sqrt{3}}{4} \times 6 \times a} = \frac{\pi}{3\sqrt{3}} = 0.60$  or 60%



**6.3 CLOSE PACKING IN THREE DIMENSIONS :**

When two dimensional packing structure are arranged one above the other, depending upon type of two dimensional arrangement in a layer, and the relative positions of spheres in above or below layer, various types of three dimensional packing results. To define 3-D lattice, six lattice parameters are required - 3 edge lengths & 3 angles.

- (i) Simple cubic packing (A A A A .....)
- (ii) Hexagonal close packing (AB AB AB .....)
- (iii) Cubic close packing or face centred cubic (ABC ABC...)

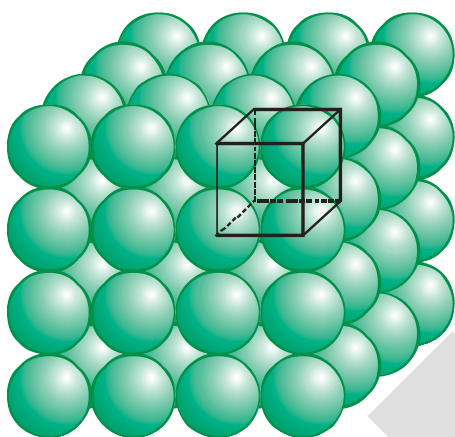
### 6.3.1 Three dimensional close packing from square two dimensional packing

#### (Simple cubic packing in three dimension)

The two dimensional square close packed layer are placed, in such a manner that spheres in each layer comes immediately on top of below layer, simple cubic packing results. Important points :

- (i) Spheres all aligned vertically and horizontally in all directions.
- (ii) The unit cell for this packing is simple cubic unit cell.
- (iii) In this packing, only 52% of available space is occupied by spheres.
- (iv) Each sphere is in contact with six spheres and hence coordination number is 6.

(v) Packing efficiency =  $\frac{1 \times \frac{4}{3} \pi r^3}{(2r)^3} = \frac{\pi}{6} \approx 0.52$



Simple cubic lattice formed by  
A A A ... arrangement

Coordination number = 6

First neighbour = 6 at a distance =  $a$

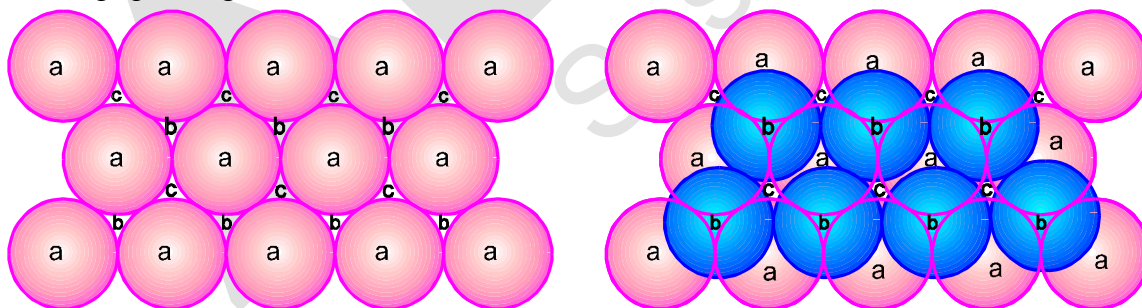
Second neighbour = 12 at  $(\sqrt{2}a)$  distance

Third neighbour = 8 at  $(\sqrt{3}a)$  distance

### 6.3.2

#### Three dimensional close packing from hexagonal two dimensional packing :

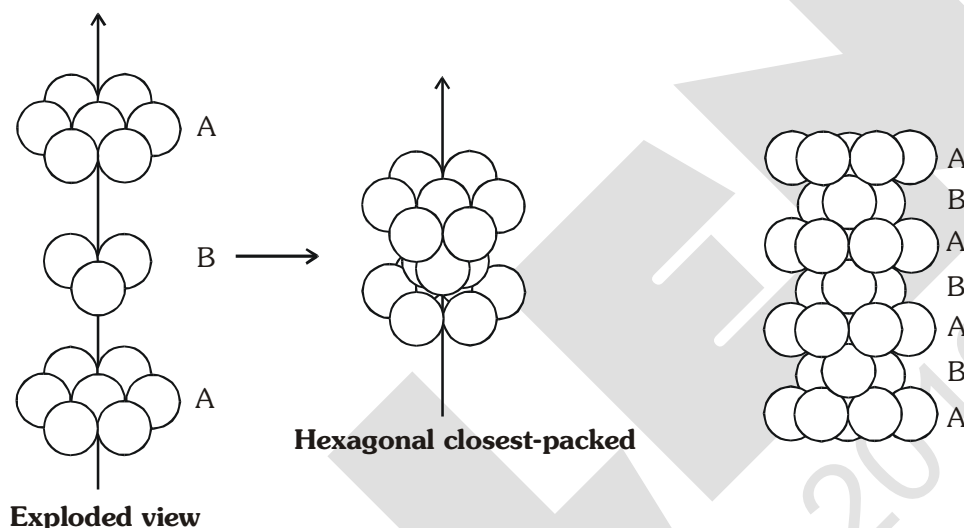
In hexagonal close packing, there are two types of the voids (open space or space left) which are divided into two sets 'b' and 'c' for convenience. The spaces marked 'c' are curved triangular spaces with tips pointing upwards whereas spaces marked 'b' are curved triangular spaces with tips pointing downwards.



Now we extend the arrangement of spheres in three dimensions by placing second close packed layer (hexagonal close packing) (B) on the first layer (A). The spheres of second layer may be placed either on space denoted by 'b' or 'c'. It may be noted that it is not possible to place spheres on both types of voids (i.e. b and c). Thus half of the voids remain unoccupied by the second layer. The second layer also have voids of the types 'b' and in order to build up the third layer, there are following ways :

**(I) Hexagonal close packing (HCP)**

- (i) In one way, the spheres of the third layer lie on the spaces of second layer (B) in such a way that they lie directly above those in the first layer (A). In other words we can say that the third layer becomes identical to the first layer. Such arrangement is called AB AB AB ....type packing or hexagonal close packing (hcp).
- (ii) Maximum possible space is occupied by spheres.
- (iii) Each sphere is touched by 12 other spheres in 3D (6 is one layer, 3 in top layer and 3 in bottom) and hence the coordination number is 12.



**(iv) Packing efficiency of HCP units**

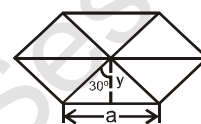
**Relation between a, b, c and R :**

$$a = b = 2R$$



$$\tan 30^\circ = \frac{a}{2 \times y}$$

So



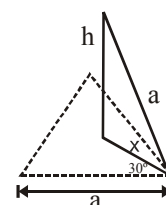
$$y = \frac{a \times \sqrt{3}}{2 \times 1} = \frac{\sqrt{3}}{2} a.$$

$$\text{Base Area} = 6 \left[ \frac{1}{2} \times \frac{a}{2} \times \frac{\sqrt{3}}{2} \times \frac{a}{2} \right] = \frac{6\sqrt{3}a^2}{4}$$

**Calculation of c :**

$$\cos 30^\circ = \frac{a}{2 \times x}$$

$$x = \frac{2a}{2 \times \sqrt{3}} = \frac{a}{\sqrt{3}}$$





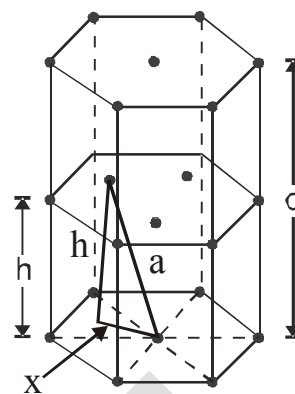
Applying pythagoras theorem :  $x^2 + h^2 = a^2$

$$\text{So } h^2 = a^2 - x^2 = a^2 - \frac{a^2}{3} = \frac{2}{3} a^2$$

$$h = \sqrt{\frac{2}{3}} a \quad \text{so} \quad c = 2h = 2\sqrt{\frac{2}{3}} a$$

So volume of hexagon = area of base  $\times$  height

$$= \frac{6\sqrt{3}}{4} \times a^2 \times 2\sqrt{\frac{2}{3}} a = \frac{6\sqrt{3}}{4} \times (2R)^2 + 2\sqrt{\frac{2}{3}} \times (2R) = 24\sqrt{2} R^3$$



(v) **Effective no. of particles (Z)**

$$Z = 3 + 2 \times \frac{1}{2} + 12 \times \frac{1}{6} = 3 + 1 + 2 = 6.$$

It must be noted that all three spheres of 'B' layer are not exactly inside the unit cell. But the contribution of three spheres are taken because the same volume of other spheres in that layer is also inside the unit cell.

(vi) **Packing efficiency** =  $\frac{6 \times \frac{4}{3} \pi R^3}{24\sqrt{2} R^3} = \frac{\pi}{3\sqrt{2}} = 0.74 \text{ or } 74\%.$

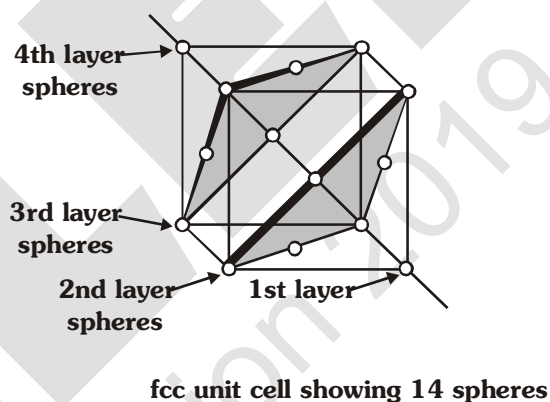
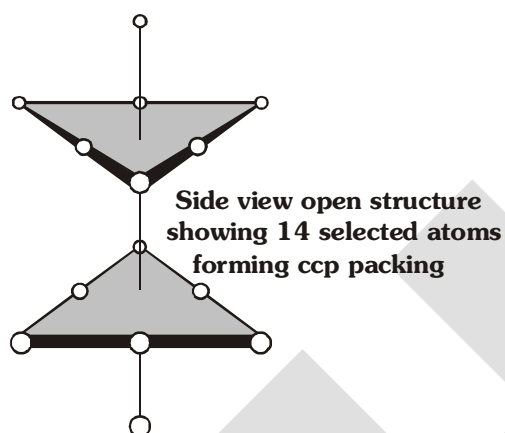
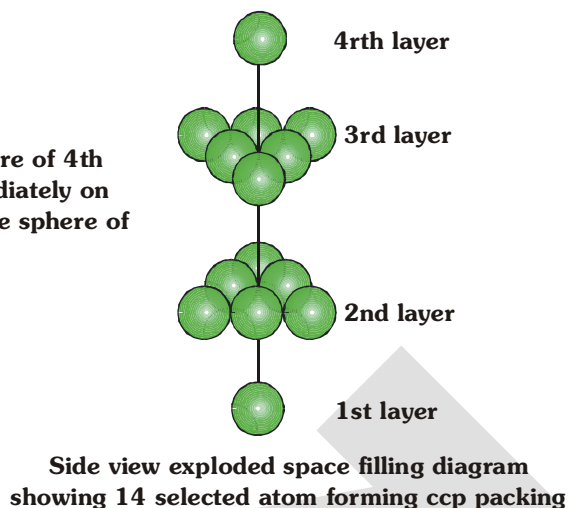
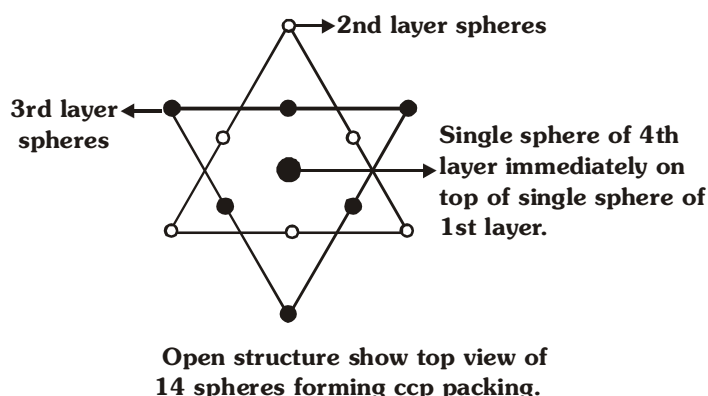
(vii) **Density (d)** =  $\frac{\text{mass}}{\text{volume}} = \left[ \frac{Z \times M}{N_A \times \text{volume}} \right]$

(II) **Cubic close packing (CCP) or face centered cubic (FCC)**

In second way, the spheres of the third layer (C) lie on the second layer (B) in such a way that they lie over the unoccupied spaces 'C' of the first layer (A). If this arrangement is continued in the same order every fourth layer becomes identical to the first. Such arrangement of particle is called ABC ABC ABC.... or cubic close packing (ccp) or face centered cubic (fcc).

It may be noted that in ccp (or fcc) structures, each sphere is surrounded by 12 spheres hence the coordination number of each sphere is 12. The spheres occupy 74% of the total volume and 26% of is the empty space in both (hcp and ccp) structures.





(i) Relation between 'a' and 'R' :

$$a \neq 2R$$

$$\sqrt{2}a = 4R \quad (\text{sphere are touching along the face diagonal})$$

(ii) Effective no. of particles per unit cell (Z)

$$Z = \frac{1}{8} \times 8 + \frac{1}{2} \times 6 = 4$$

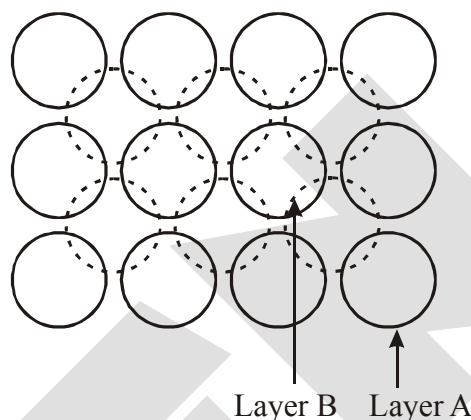
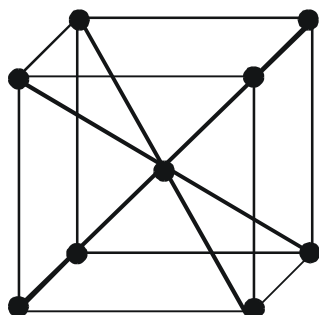
(iii) Packing fraction :

$$\text{P.F.} = \frac{4 \times \frac{4}{3} \pi R^3}{4 \times 4 \times 4 R^3} \times \sqrt{2} \times 2 = \frac{\pi}{3\sqrt{2}} = 0.74 \text{ or } 74\%$$

(iv) Density (d) =  $\frac{Z \times M}{N_A \times a^3}$

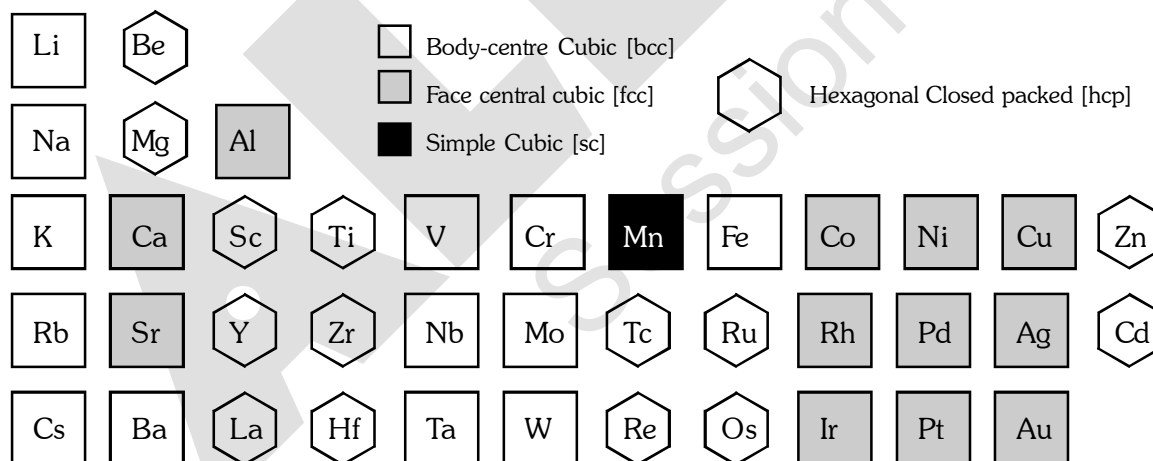
### 6.3.3 Body centred cubic (bcc):

There is another possible arrangement of packing of spheres known as body centred cubic (bcc) arrangement. This arrangement is observed in square close packing in which there is suitable space between the spheres in each layer. In bcc arrangement, the spheres of the second layer lie at the space (hollows or voids) in the first layer.



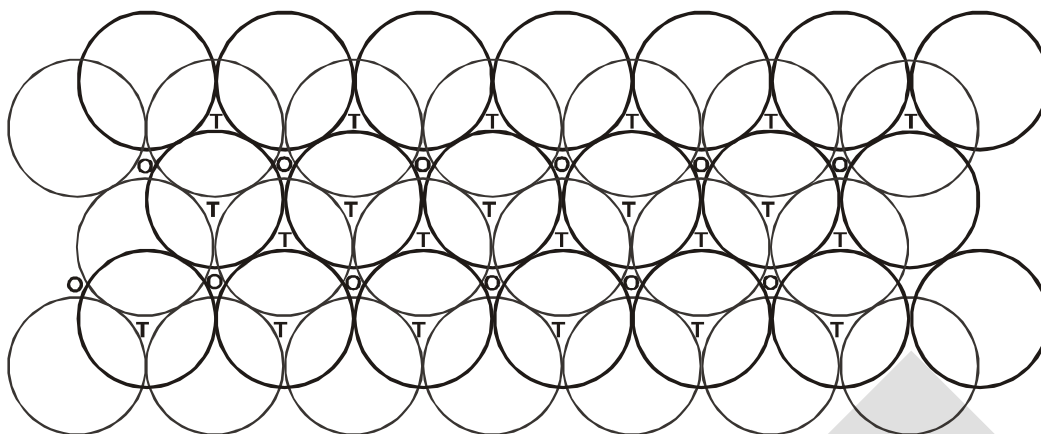
Thus each sphere of the second layer touches four spheres of the first layer. Now spheres of the third layer are placed exactly about the spheres of first layer. In this way each sphere of the second layer touches eight spheres (four of 1st layer and four of IIIrd layer). Therefore coordination number of each sphere is 8 in bcc sturcture. The spheres occupy 68% of the total volume 32% of the volume is the empty space.

## 7. STRUCTURES OF VARIOUS ELEMENTS



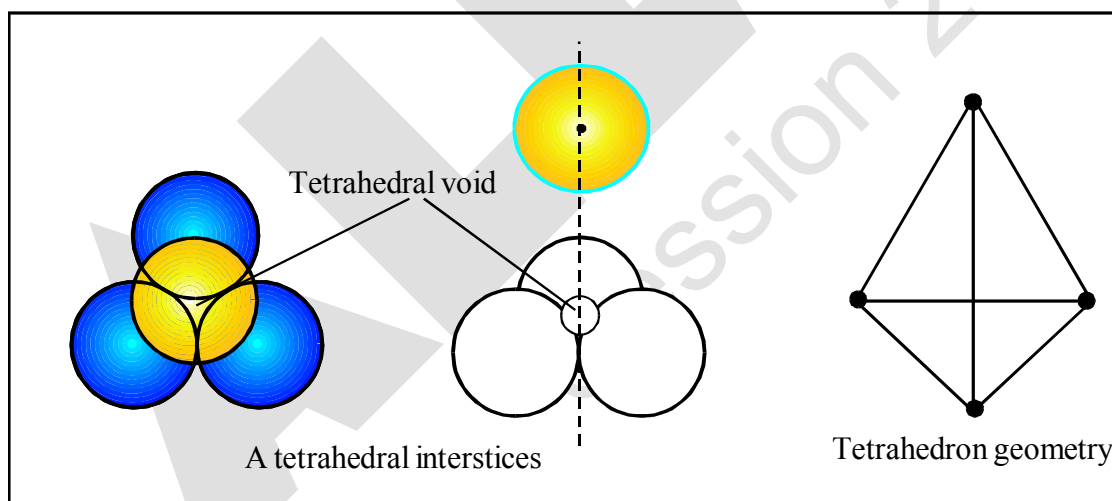
## 8. INTERSTICES OR VOIDS OR HOLES IN CRYSTALS

It has been shown that the particles are closely packed in the crystals even though there is some empty space left in between the spheres. This is known as interstices (or interstitial site or hole or empty space or voids). In three dimensional close packing (CCP & HCP) the interstices are of two types :  
(i) tetrahedral voids and (ii) octahedral voids.



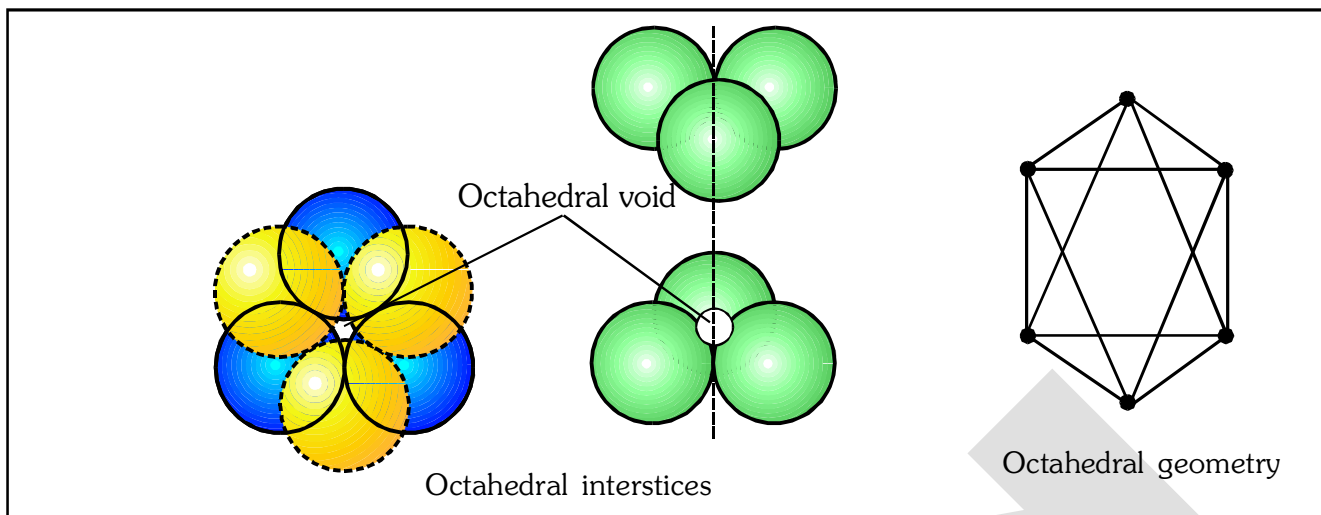
A stack of two layers of close packed spheres and voids generated in them. T = Tetrahedral void; O = Octahedral void

- (i) **Tetrahedral voids :** We have seen that in hexagonal close packing (hcp) and cubic close packing (ccp), each sphere of second layer touches with three spheres of first layer. Thus, they leave a small space in between which is known as **tetrahedral site or interstices**. In another words, the vacant space between 4 touching spheres is called as tetrahedral void. Since a sphere touches three spheres in the below layer and three spheres in the above layer hence there are two tetrahedral sites associated with one sphere. It may be noted that a tetrahedral site does not mean that the site is tetrahedral in geometry but it means that this site is surrounded by four spheres and the centres of these four spheres lie at the apices of a regular tetrahedron.



- (ii) **Octahedral voids :** Hexagonal close packing (hcp) and cubic close packing (ccp) also form another type of interstices (or site), which is called octahedral site (or interstices). In another words, the vacant space between 6 touching spheres is called as octahedral void.

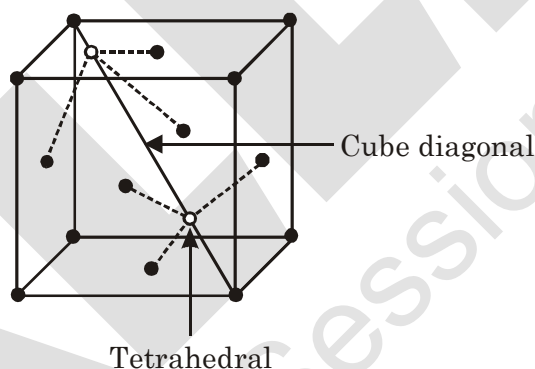
In the figure two layers of close packed spheres are shown. The spheres of first layer are shown by full circles while that of second layer by dotted circles. Two triangles are drawn by joining the centres of three touching spheres of both the layers.



The apices of these triangles point are in opposite directions. On super imposing these triangles on one another, an octahedral site is created. It may be noted that an octahedral site does not mean that the hole is octahedral in shape but it means that this site is surrounded by six nearest neighbour lattice points arranged octahedrally.

### 8.1 POSITIONS OF TETRAHEDRAL VOIDS IN AN FCC UNIT CELL :

In FCC, one corner and its three face centred atom of faces meeting at that corner form a tetrahedral void. In FCC, two tetrahedral voids are obtained along one cube diagonal. So in FCC 8 tetrahedral voids are present.



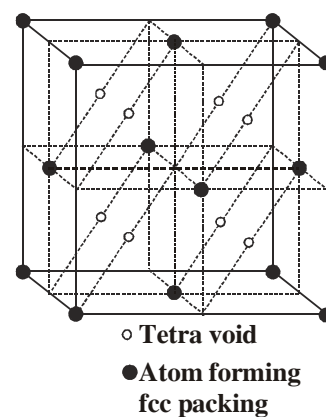
Alternatively, the centre of tetrahedral void is located on the centre

of body diagonal of each small cube of volume  $\left(\frac{a^3}{8}\right)$ .

$$\text{Total number of particles per unit cell} = \frac{1}{2} \times 6 + 8 \times \frac{1}{8} = 4$$

Total number of tetrahedral void = 8

$\therefore$  Effective number of tetrahedral void per particle = 2.



## 8.2 POSITION OF OCTAHEDRAL VOID IN FCC UNIT CELL :

Position of octahedral void is at mid-point of each edge

(total 12 edges in a cube) and at the centre of cube.

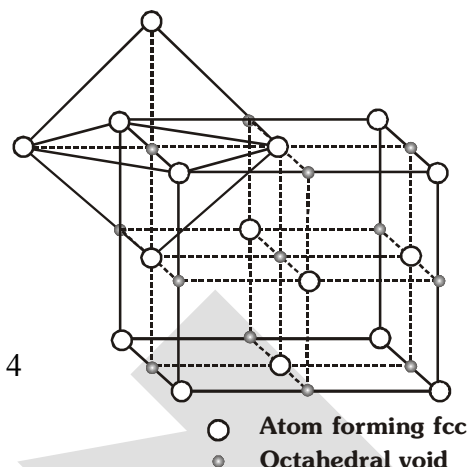
Each octahedral void located at mid point of edge contributes  $\frac{1}{4}$  to the unit cell. The octahedral void situated at the centre contributes 1.

In FCC, total number of octahedral voids are

$$\begin{array}{ccc} (1 \times 1) & + & (12 \times \frac{1}{4}) = 1 + 3 = 4 \\ \text{(Cube centre)} & & \text{(edge)} \end{array}$$

In FCC, number of particles = 4

$\therefore$  Effective number of octahedral voids per particle = 1



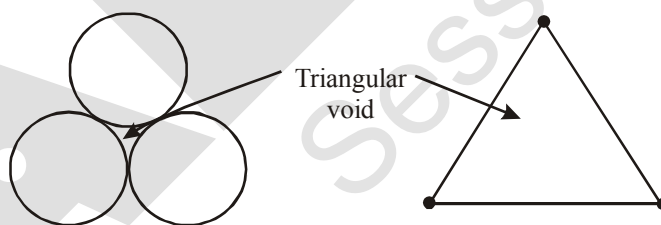
## 8.3 POSITION OF TETRAHEDRAL AND OCTAHEDRAL VOID IN HCP:

- Above & below each sphere, there is a tetrahedral void, hence number of tetrahedral void per unit cell = 12
- Other than TV, all voids are OV & number of OV per unit cell =  $2 \times 3 = 6$

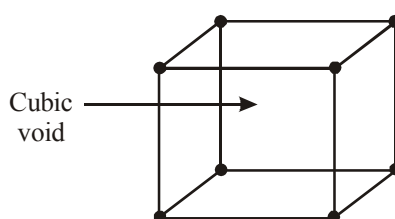
**Note :** In any closed packing of maximum efficiency, there are two TV & one OV per particle

## 8.4 Triangular and cubic voids :

- Triangular void :** It is formed by three spheres in a plane.



- Cubic void :** It is formed in simple cubic unit cell by eight spheres at the corners of cube.



## 9. CRYSTAL OF DIAMOND

The crystal is FCC for C atom & alternate tetrahedral voids are also occupied by carbon atoms.

$$* \quad Z = \frac{1}{8} \times 8 + 6 \times \frac{1}{2} + 4 = 8$$

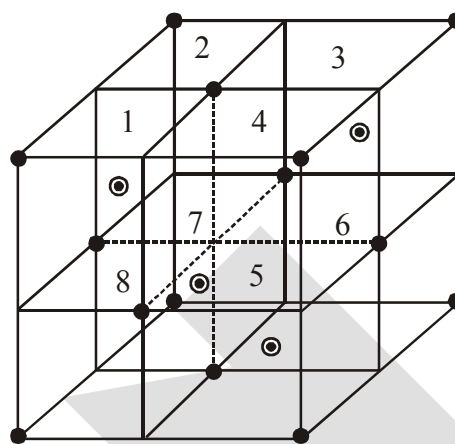
$$* \quad \text{CN} = 4$$

$$* \quad \frac{\sqrt{3}a}{4} = 2r = d_{\text{C-C}}$$

$$* \quad \text{Number of C-C bonds/unit cell} = 4 \times 4 = 16$$

$$* \quad \text{Number of C-C bonds/C-atom} = \frac{16}{8} = 2$$

$$* \quad \text{PE} = \frac{8 \times \frac{4}{3} \pi r^2}{\left(\frac{8r}{\sqrt{3}}\right)^3} = \frac{\sqrt{3}\pi}{16} \approx 0.34 \text{ or } 34\%$$



## CLASS ILLUSTRATION

**Ex.6** A solid crystallises in close packing for 'P' atoms and 25% of tetrahedral voids are occupied by 'Q' atoms. What is the simplest formula of solid ?

**Sol.**  $Z_p = 1(\text{say})$

$$Z_Q = \frac{25}{100} \times 2 = \frac{1}{2}$$

$$\therefore \text{Simplest formula of solid} = \text{PQ}_{1/2} = \text{P}_2\text{Q}$$

**Ex.7** Calculate the radius ( $r$ ) of largest sphere which may be fitted in the (i) triangular voids (ii) tetrahedral voids (iii) octahedral voids (iv) cubic voids made by identical spheres of radius, ' $R$ ', without disturbing the crystal.

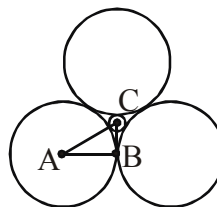
**Sol.** (i)  $AB = R$

$$AC = R + r$$

$$\angle BAC = 30^\circ$$

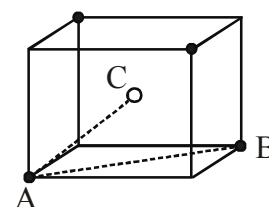
$$\text{Now, } \cos 30^\circ = \frac{AB}{AC} \Rightarrow \frac{\sqrt{3}}{2} = \frac{R}{R+r}$$

$$r = \left( \frac{2}{\sqrt{3}} - 1 \right) R = 0.155R$$



(ii)  $AB = \sqrt{2}a = 2R$

$$AC = \frac{\sqrt{3}a}{2} = R + r$$



$$\text{Now, } \frac{R+r}{R} = \frac{\sqrt{3}}{\sqrt{2}}$$

$$\therefore r = \left( \sqrt{\frac{3}{2}} - 1 \right) R = 0.225R$$

(iii)  $AB = R$

$$AC = R + r$$

$$\angle BAC = 45^\circ$$

$$\text{Now, } \cos 45^\circ = \frac{AB}{AC} \Rightarrow \frac{1}{\sqrt{2}} = \frac{R}{R+r}$$

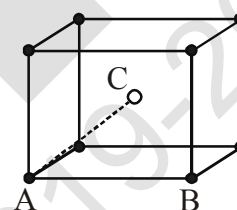
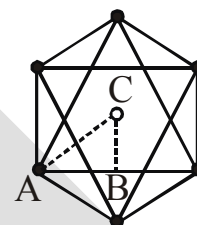
$$\therefore r = (\sqrt{2} - 1)R = 0.414R$$

(iv)  $AB = a = 2R$

$$AC = \frac{\sqrt{3}a}{2} = R + r$$

$$\text{Now, } \frac{R+r}{R} = \sqrt{3}$$

$$\therefore r = (\sqrt{3} - 1)R = 0.732R$$



**Ex.8** An element (molar mass = 60 gm/mole) crystallises in CCP lattice. If density is 6.25 gm/cm<sup>3</sup> and the distance between next nearest neighbour is  $d\text{\AA}$ , then the value of 'd' is ( $N_A = 6 \times 10^{23}$ ).

**Sol.** Ans.(4)

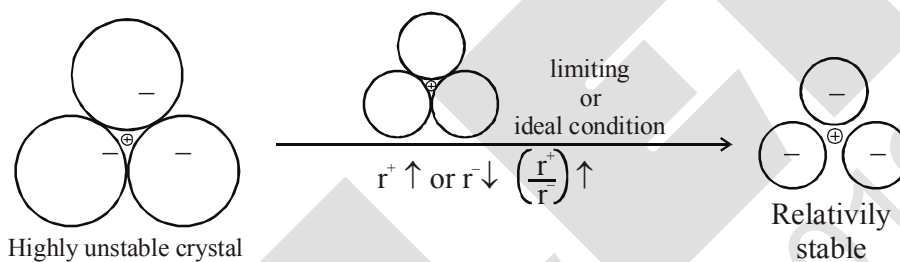
$$d = \frac{ZM}{N_A \cdot a^3}$$

$$6.25 = \frac{4 \times 60}{6 \times 10^{23} \times a^3} \Rightarrow a = 4 \times 10^{-8} \text{ cm} = 4\text{\AA}.$$

## 10 PACKING IN IONIC SOLID

- (i) Normally anions are bigger than cations, hence ionic solid are considered as the packing of anions and cations are supposed to occupy the voids.
- (ii) Oppositely charged particles should lie closer and similarly charged particles should lie away from each other.
- (iii) Each ion tend to maximise its coordination number (Number of oppositely charged ions around it).

Point (ii) and (iii) contradict each other because on increase the CN, the repulsion between like charges will also increases. Hence, in all the ionic solids, there must be a balance with the help of relative size of ions to ensure maximum CN and minimum repulsion between like charges.

10.1 LIMITING OR IDEAL RADIUS RATION  $\left(\frac{r^+}{r^-}\right)$ :

The minimum  $\frac{r^+}{r^-}$  values for the existence of a cation in a particular void is called **limiting radius ratio** for that void.

With the increase in radius ratio, space between anion will increase & hence the cation may tend for higher coordination number.

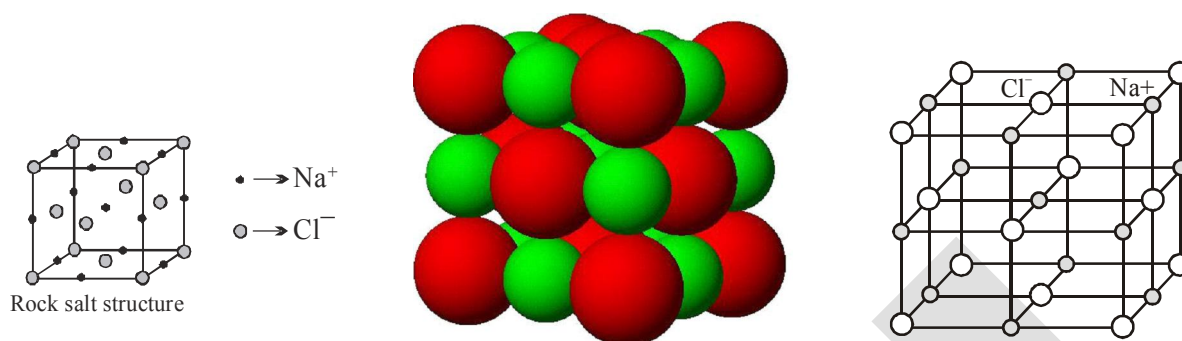
| Voids       | CN | Limiting $r^+/r^-$ | Range of $r^+/r^-$ |
|-------------|----|--------------------|--------------------|
| Triangular  | 3  | 0.155              | 0.155 – 0.225      |
| Tetrahedral | 4  | 0.225              | 0.225 – 0.414      |
| Octahedral  | 6  | 0.414              | 0.414 – 0.732      |
| Cubic       | 8  | 0.732              | 0.732 – 1.000      |

\* For values lesser than 0.155, crystal will not exist.



## 10.2 TYPES OF IONIC STRUCTURES:

### 10.2.1 Rock salt structure (NaCl) :



The bigger  $\text{Cl}^-$  forms cubic close packing and small  $\text{Na}^+$  occupy positions of all octahedral voids. The radius ratio  $\frac{r^+}{r^-}$  lie in the range 0.414 – 0.732.

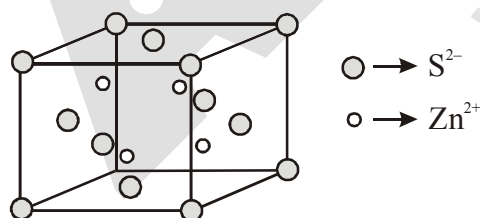
- (i) Each  $\text{Na}^+$  is surrounded by six  $\text{Cl}^-$  and each  $\text{Cl}^-$  is surrounded by six  $\text{Na}^+$  ion. [6:6 coordination]
- (ii) No. of  $\text{Na}^+$  and  $\text{Cl}^-$  in each unit cell is 4.
- (iii) Number of formula units of NaCl per unit cell is equal to 4.

(iv) The density of NaCl crystal is given by  $d = \left( \frac{4 \times M_{\text{NaCl}}}{N_A \times a^3} \right)$

(v) The edge length of NaCl unit cell is given by  $(2r^+ + 2r^-) \Rightarrow \frac{a}{2} = r^+ + r^-$

### 10.2.2 Zinc blende (sphalerite) structure (ZnS) :

Larger ion ( $\text{S}^{2-}$ ) forming ccp arrangement and smaller ion ( $\text{Zn}^{2+}$ ) filling half or alternate tetrahedral voids



Zinc blende structure

(i) C.N. of  $\text{Zn}^{2+} = 4$  ; C.N. of  $\text{S}^{2-} = 4$  [4 : 4 coordination]

(ii) Formula units of ZnS per unit cell = 4. (iii)  $d_{\text{ZnS}} = \frac{4 \times M_{\text{ZnS}}}{N_A \times a^3}$  (iv)  $r_{\text{Zn}^{2+}} + r_{\text{S}^{2-}} = \frac{a\sqrt{3}}{4}$

**10.2.3 Cesium chloride structure (CsCl) :**

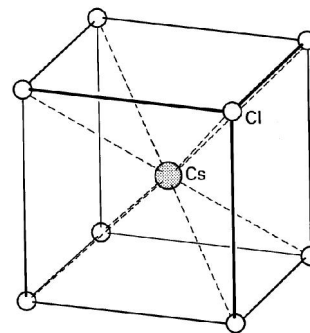
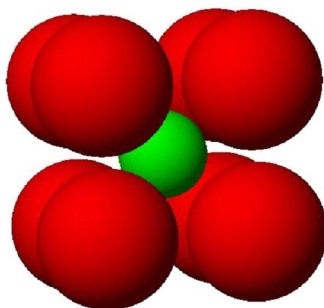
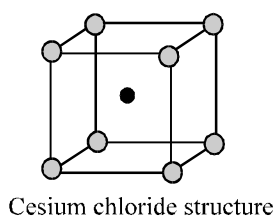
$\text{Cl}^-$  at the corners of cube and  $\text{Cs}^+$  in the center (cubic void).

(i) C.N. of  $\text{Cs}^+ = 8$  ; C.N. of  $\text{Cl}^- = 8$  [8 : 8 coordination]

(ii) Formula units of CsCl per unit cell = 1

$$\text{(iii)} \quad d_{\text{CsCl}} = \frac{M_{\text{CsCl}}}{N_A \times a^3}$$

$$\text{(iv)} \quad r_{\text{Cs}^+} + r_{\text{Cl}^-} = \frac{a\sqrt{3}}{2} \Rightarrow \boxed{r^+ + r^- = \frac{a\sqrt{3}}{2}}$$

**10.2.4 Fluorite structure ( $\text{CaF}_2$ ) :**

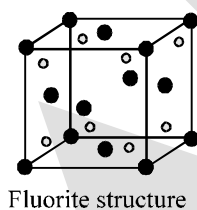
$\text{Ca}^{2+}$  forming ccp arrangement and  $\text{F}^-$  filling all tetrahedral voids.

(i) C.N. of  $\text{F}^- = 4$  ; C.N. of  $\text{Ca}^{2+} = 8$  [8 : 4 coordination]

(ii) Formula units of  $\text{CaF}_2$  per unit cell = 4

$$\text{(iii)} \quad d_{\text{CaF}_2} = \frac{4 \times M_{\text{CaF}_2}}{N_A \times a^3}$$

$$\text{(iv)} \quad r_{\text{Ca}^{2+}} + r_{\text{F}^-} = \frac{a\sqrt{3}}{4}$$

**10.2.5 Antifluorite structure ( $\text{Li}_2\text{O}$ ) :**

$\text{O}^{2-}$  ion forming ccp and  $\text{Li}^+$  taking all tetrahedral voids.

(i) C.N. of  $\text{Li}^+ = 4$

C.N. of  $\text{O}^{2-} = 8$

(ii) Formula units of  $\text{Li}_2\text{O}$  ; per unit cell = 4

$$\text{(iii)} \quad d_{\text{Li}_2\text{O}} = \frac{4 \times M_{\text{Li}_2\text{O}}}{N_A \times a^3} \quad \text{(iv)} \quad r_{\text{Li}^+} + r_{\text{O}^{2-}} = \frac{a\sqrt{3}}{4}$$

**10.2.6 Corundum Structure ( $\text{Al}_2\text{O}_3$ ) :**

$\text{O}^{2-}$  forming hcp and  $\text{Al}^{3+}$  filling 2/3 octahedral voids.

### 10.2.7 Rutile structure ( $\text{TiO}_2$ ) :

$\text{O}^{2-}$  forming hcp while  $\text{Ti}^{4+}$  ions occupy half of the octahedral voids.

### 10.2.8 Pervoskite structure ( $\text{CaTiO}_3$ ) :

$\text{Ca}^{2+}$  in the corner of cube,  $\text{O}^{2-}$  at the face center and  $\text{Ti}^{4+}$  at the centre of cube.

### 10.2.9 Spinel and inverse spinel structure ( $\text{MgAl}_2\text{O}_4$ ) :

$\text{O}^{2-}$  forming fcc,  $\text{Mg}^{2+}$  filling  $1/8$  of tetrahedral voids and  $\text{Al}^{3+}$  taking half of octahedral voids.

In an inverse spinel structure,  $\text{O}^{2-}$  ion form FCC lattice,  $\text{A}^{2+}$  ions occupy  $1/8$  of the tetrahedral voids and trivalent cation occupies  $1/8$  of the tetrahedral voids and  $1/4$  of the octahedral voids.

**Ex.9** A solid  $\text{A}^+\text{B}^-$  has NaCl type close packed structure. If the anion has a radius of 250 pm, what should be the ideal radius for the cation ? Can a cation  $\text{C}^+$  having a radius of 180 pm be slipped into the tetrahedral site of the crystal  $\text{A}^+\text{B}^-$  ? Give reason for your answer.

**Sol.** In  $\text{Na}^+\text{Cl}^-$  crystal each  $\text{Na}^+$  ion is surrounded by 6  $\text{Cl}^-$  ions and vice versa. Thus  $\text{Na}^+$  ion is placed in octahedral hole.

The limiting radius ratio for octahedral site = 0.414

$$\text{or } \frac{r_{\text{A}^+}}{R_{\text{B}^-}} = \frac{r}{R} = 0.414$$

Given that radius of anion ( $\text{B}^-$ )  $R = 250$  pm

i.e. radius of cation ( $\text{A}^+$ )  $r = 0.414 R = 0.414 \times 250$  pm

or  $r = 103.5$  pm

Thus ideal radius for cation ( $\text{A}^+$ ) is  $r = 103.5$  pm.

We know that  $(r/R)$  for tetrahedral hole is 0.225.

$$\therefore \frac{r}{R} = 0.225$$

$$\text{or } r = 0.225 R = 0.225 \times 250 = 56.25 \text{ pm}$$

Thus ideal radius for cation is 56.25 pm for tetrahedral hole. But the radius of  $\text{C}^+$  is 180 pm. It is much larger than ideal radius i.e. 56.25 pm. Therefore we can not slip cation  $\text{C}^+$  into the tetrahedral site.

**Ex.10** A compound forms hexagonal close-packed structure. What is the total number of voids in 0.5 mole of it? How many of these are tetrahedral voids?

**Sol.** Since, for every atom forming hcp structure there are two tetrahedral voids and one octahedral void.

Total voids =  $3 \times 0.5 = 1.5$  mol and total tetrahedral void =  $2 \times 0.5 = 1$  mol.

**Ex.11** A compound is formed by two elements M and N. The element N forms ccp and atoms of M occupy  $1/3$ rd of tetrahedral voids. What is the formula of the compound?

**Sol.** In one unit cell of ccp, no. of N = 4 ; total no. of tetrahedral void = 8 ; occupied tetrahedral void by M =  $8/3$  ; Empirical formula :  $\text{N}_4\text{M}_{8/3} = \text{N}_3\text{M}_2$ .

## 11. IMPERFECTIONS IN SOLIDS

Although crystalline solids have short range as well as long range order in the arrangement of their constituent particles, yet crystals are not perfect. Usually a solid consists of an aggregate of large number of small crystals. These small crystals have defects in them. This happens when crystallisation process occurs at fast or moderate rate. Single crystals are formed when the process of crystallisation occurs at extremely slow rate. Even these crystals are not free of defects.

The defects are basically irregularities in the arrangement of constituent particles. Broadly speaking, the defects are of two types, namely, **point defects** and **line defects**. Point defects are the irregularities or deviations from ideal arrangement around a point or an atom in a crystalline substance, whereas the line defects are the irregularities or deviations from ideal arrangement in entire rows of lattice points. These irregularities are called crystal defects. We shall confine our discussion to point defects only.

### 11.1 Types of Point Defects

Point defect can be classified into three types:

- (i) Stoichiometric defects
- (ii) Non-stoichiometric defects
- (iii) Impurity added defect

#### (i) Stoichiometric Defect

These are the point defect that do not disturb the stoichiometry of the solid. They are also called **intrinsic** or **thermodynamic defects**. Basically these are of two types; vacancy defects and interstitial defect.

##### (a) Vacancy Defect :

When some of the lattice sites are vacant, the crystal is said to have vacancy defect. This results in decrease in density of the substance. This defect can also develop when a substance is heated.

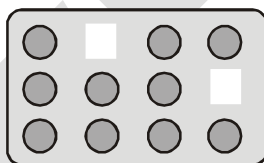


Fig. : Vacancy defects

**(b) Interstitial Defect :** When some constituent particles (atoms or molecules) occupy an interstitial site, the crystal is said to have interstitial defect. This defect increases the density of the substance.

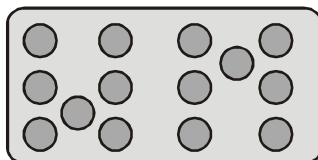


Fig. : Interstitial defects

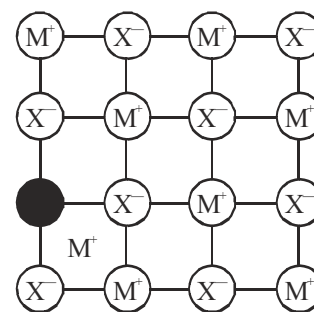
Vacancy and interstitial defects as explained above can be shown by non-ionic solids. Ionic solids must always maintain electrical neutrality. Rather than simple vacancy or interstitial defects, they show these defects as **Frenkel and Schottky defects**.

**(c) Frenkel Defect :** This defect is shown by ionic solids.

The smaller ion (usually cation) is delocalised from its normal site to an interstitial site. It creates a vacancy defect at its original site and an interstitial defect at its new location.

Frenkel defect is also called **dislocation defect**. It does not change the density of the solid.

Frenkel defect is shown by ionic substance in which there is a large difference in the size of ions, for example, ZnS, AgCl, AgBr and AgI due to small size of  $\text{Zn}^{2+}$  and  $\text{Ag}^+$  ions.



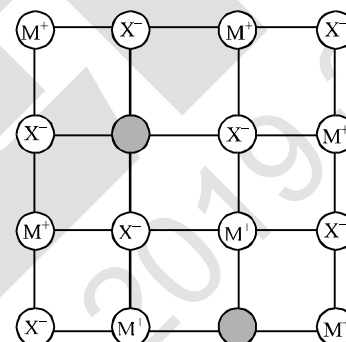
Frenkel Defect

**Influences :** Makes solid crystals good conductor. In Frenkel defect, ions in interstitial sites increases the dielectric constant.

**(d) Schottky Defect :** It is basically a vacancy defect in ionic solids. In order to maintain electrical neutrality, the number of missing cations and anions are equal (in stoichiometric ratio)

Like simple vacancy defect, Schottky defect also decreases the density of the substance. Number of such defects in ionic solids is quite significant. For example, in NaCl there are approximately,

$10^6$  Schottky pairs per  $\text{cm}^3$  at room temperature. In  $1 \text{ cm}^3$  there are about  $10^{22}$  ions. Thus, there is one Schottky defect per  $10^{16}$  ions. Schottky defect is shown by ionic substances in which the cation and anion are of almost similar sizes. For example, NaCl, KCl, CsCl and AgBr. It may be noted that AgBr shows both, Frenkel as well as Schottky defects.



Schottky Defect

**Influence :** The presence of large number of schottky defects in crystal results in significant decrease in its density.

## (ii) Non-Stoichiometric Defects

The defects discussed so far do not disturb the stoichiometry of the crystalline substance. However, a large number of non-stoichiometric inorganic solids are known which contain the constituent elements in non-stoichiometric ratio due to defects in their crystal structures. These defects are of two types:

- Metal excess defect.
- Metal deficiency defect.

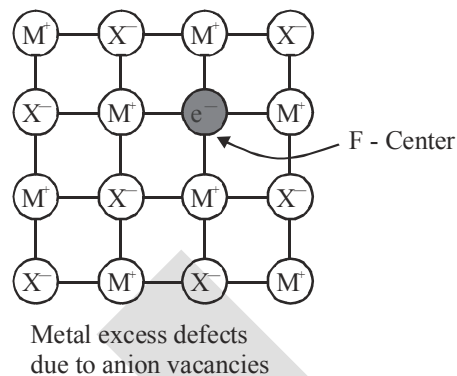
## (a) Metal Excess Defect

## (I) Metal excess defect due to anionic vacancies :

Alkali halides like NaCl and KCl show this type of defect. When crystals of NaCl are heated in an atmosphere of sodium vapour, the sodium atoms are deposited on the surface of the crystal. The  $\text{Cl}^-$  ions diffuse to the surface of the crystal and combine with Na atoms to give NaCl. This happens by loss of electron by sodium atoms to form  $\text{Na}^+$  ions.

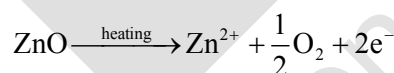
The released electrons diffuse into the crystal and occupy anionic sites. As a result the crystal now has an excess of sodium. The anionic sites occupied by unpaired electrons are called **F-centres** (from the German word *Farbenzenter* for colour centre).

They impart yellow colour to the crystals of NaCl. The colour results by excitation of these electrons when they absorb energy from the visible light falling on the crystals. Similarly, excess of lithium makes LiCl crystals pink and excess of potassium makes KCl crystals violet (or lilac).

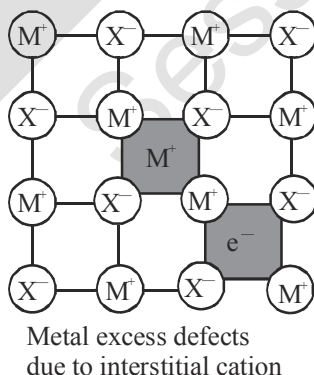


## (II) Metal excess defect due to the presence of extra cations at interstitial sites :

Zinc oxide is white in colour at room temperature. On heating it loses oxygen and turns yellow.



Now there is excess of zinc in the crystal and its formula becomes  $\text{Zn}_{1+x}\text{O}$ . The excess  $\text{Zn}^{2+}$  ions move to interstitial sites and the electrons to neighbouring interstitial sites.

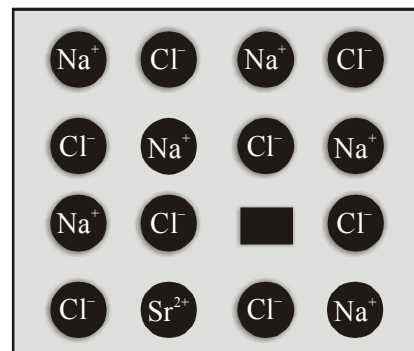


## (b) Metal Deficiency Defect

There are many solids which are difficult to prepare in the stoichiometric composition and contain less amount of the metal as compared to the stoichiometric proportion. A typical example of this type is FeO which is mostly found with a composition of  $\text{Fe}_{0.95}\text{O}$ . It may actually range from  $\text{FeO}_{0.93}$  to  $\text{Fe}_{0.96}\text{O}$ . In crystals of FeO, some  $\text{Fe}^{2+}$  cations are missing and the loss of positive charge is made up by the presence of required number of  $\text{Fe}^{3+}$  ions.

**(iii) Impurity Defects**

If molten NaCl containing a little amount of  $\text{SrCl}_2$  is crystallised, some of the sites of  $\text{Na}^+$  ions are occupied by  $\text{Sr}^{2+}$ . Each  $\text{Sr}^{2+}$  replaces two  $\text{Na}^+$  ions. It occupies the site of one ion and the other site remains vacant. The cationic vacancies thus produced are equal in number to that of  $\text{Sr}^{2+}$  ions. Another similar example is the solid solution of  $\text{CdCl}_2$  and  $\text{AgCl}$ .



Introduction of cation vacancy in NaCl by substitution of  $\text{Na}^+$  by  $\text{Sr}^{2+}$

- Note:** (i) As temperature increases, no. of defects increases exponentially.  
 (ii) For defect formation :  $\Delta H > 0$ ,  $\Delta S > 0$   
 $\therefore$  More spontaneous at higher temperatures.  
 (iii) No matter how many imperfections are present in a crystal, it is always electrically neutral (no net charge).

**12. ELECTRICAL PROPERTIES**

Solids exhibit an amazing range of electrical conductivities, extending over 27 orders of magnitude ranging from  $10^{-20}$  to  $10^7 \text{ ohm}^{-1} \text{ m}^{-1}$ . Solids can be classified into three types on the basis of their conductivities.

- (i) **Conductors** : The solids with conductivities ranging between  $10^4$  to  $10^7 \text{ ohm}^{-1} \text{ m}^{-1}$  are called conductors. Metals having conductivities in the order of  $10^7 \text{ ohm}^{-1} \text{ m}^{-1}$  are good conductors.  
 (ii) **Insulators** : These are the solids with very low conductivities ranging between  $10^{-20}$  to  $10^{-10} \text{ ohm}^{-1} \text{ m}^{-1}$ .  
 (iii) **Semiconductors** : These are the solids with conductivities in the intermediate range from  $10^{-6}$  to  $10^4 \text{ Ohm}^{-1} \text{ m}^{-1}$ .

**12.1 : Conduction of Electricity in Metals**

A conductor may conduct electricity through movement of electrons or ions. Metallic conductors belong to the former category and electrolytes to the latter.

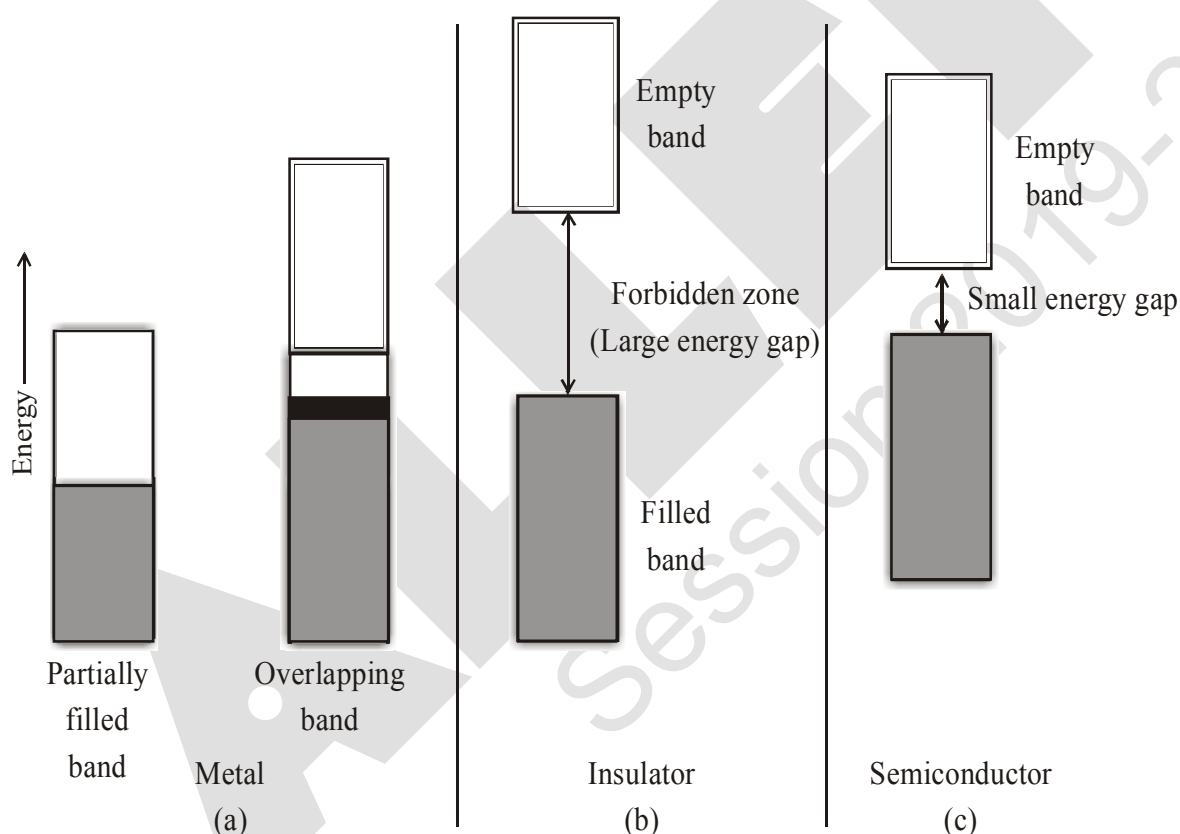
Metals conduct electricity in solid as well as molten state. The conductivity of metals depend upon the number of valence electrons available per atom. The atomic orbitals of metal atoms form molecular orbitals which are so close in energy to each other as to form a band. If this band is partially filled or it overlaps with a higher energy unoccupied conduction band, then electrons can flow easily under an applied electric field and the metal shows conductivity.

## 12.2 : Insulator :

If the gap between filled valence band and the next higher unoccupied band (conduction band) is large, electron cannot jump to it and such a substance has very small conductivity and it behaves as an insulator.

## 12.3 : Conduction of Electricity in Semi-conductor

In case of semiconductors, the gap between the valence band and conduction band is small. Therefore, some electrons may jump to conduction band and show some conductivity. Electrical conductivity of semiconductors increases with rise in temperature, since more electrons can jump to the conduction band. Substances like silicon and germanium show this type of behaviour and are called **intrinsic semiconductors**.



**Distinction among (a) metals (b) insulators and (c) semiconductors.**

**In each case, an unshaded area represents a conduction band.**

The conductivity of these intrinsic semiconductors is too low to be of practical use. Their conductivity is increased by adding an appropriate amount of suitable impurity. This process is called **doping**. Doping can be done with an impurity which is electron rich or electron deficient as compared to the intrinsic semiconductor silicon or germanium. Such impurities introduce *electrical defect* in them.

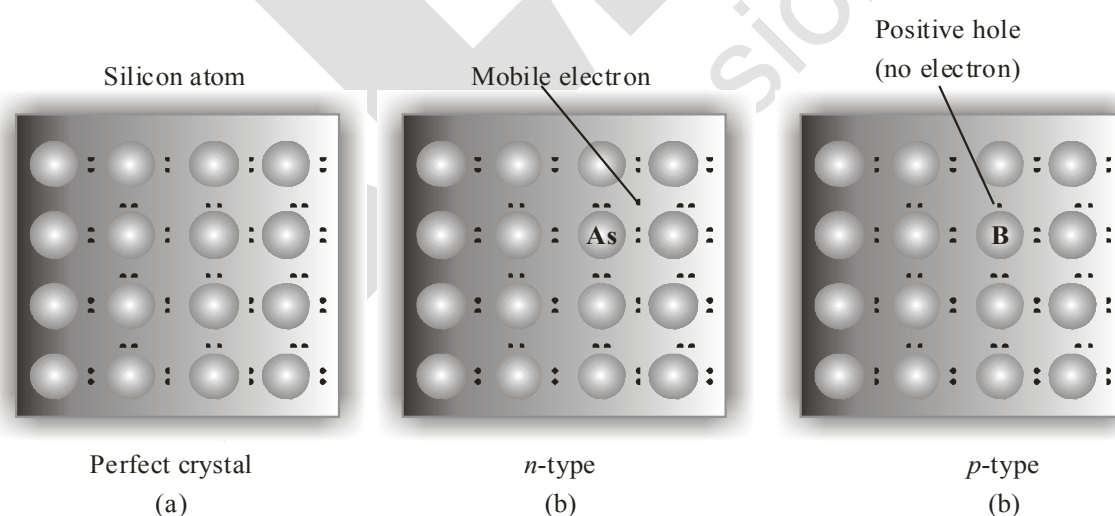


(a) Electron – rich impurities

Silicon and germanium belong to group 14 of the periodic table and have four valence electrons each. In their crystals each atom forms four covalent bonds with its neighbours. When doped with a group 15 element like P or As, which contains five valence electrons, they occupy some of the lattice sites in silicon or germanium crystal. Four out of five electrons are used in the formation of four covalent bonds with the four neighbouring silicon atoms. The fifth electron is extra and becomes delocalised. These delocalised electrons increase the conductivity of doped silicon (or germanium). Here the increase in conductivity is due to the negatively charged electron, hence silicon doped with electron-rich impurity is called ***n-type semiconductor***.

(b) Electron – deficit impurities

Silicon or germanium can also be doped with a group 13 element like B, Al or Ga which contains only three valence electrons. The place where the fourth valence electron is missing is called ***electron hole or electron vacancy***. An electron from a neighbouring atom can come and fill the electron hole, but in doing so it would leave an electron hole at its original position. If it happens, it would appear as if the electron hole has moved in the direction opposite to that of the electron that filled it. Under the influence of electric field, electrons would move towards the positively charged plate through electronic holes, but it would appear as if electron holes are positively charged and are moving towards negatively charged plate. This type of semi conductors are called ***p-type semiconductors***.



***Creation of n-type and p-type semi conductors by doping groups 13 and 15 elements***

(c) **Applications of n-type and p-type semiconductors**

Various combinations of *n*-type and *p*-type semiconductors are used for making electronic components. Diode is a combination of *n*-type and *p*-type semiconductor and is used as a rectifier. Transistors are made by sandwiching a layer of one type of semiconductor between two layers of the other type of semiconductor. *npn* and *pnp* type of transistors are used to detect or amplify radio or audio signals. The solar cell is an efficient photo-diode used for conversion of light energy into electrical energy.

Germanium and Silicon are group 14 elements and therefore, have a characteristic valency of four and form four bonds as in diamond. A large variety of solid state materials have been prepared by combination of group 13 and 15 or 12 and 16 to simulate average valence of four as in Ge or Si. Typical compounds of groups 13-15 are InSb, AlP and GaAs. Gallium arsenide (GaAs) semiconductor have very fast response and have revolutionised the design of semiconductor devices. ZnS, CdS, CdSe and HgTe are examples of groups 12-16 compounds. In these compounds, the bonds are not perfectly covalent and the ionic character depends on the electronegativities of the two elements.

It is interesting to learn that transition metal oxides show marked differences in electrical properties.  $\text{TiO}$ ,  $\text{CrO}_2$  and  $\text{ReO}_3$  behave like metals. Rhenium oxide,  $\text{ReO}_3$  is like metallic copper in its conductivity and appearance. Certain other oxides like  $\text{VO}$ ,  $\text{VO}_2$ ,  $\text{VO}_3$  and  $\text{TiO}_3$  show metallic or insulating properties depending on temperature.

**13. MAGNETIC PROPERTIES :**

Every substance has some magnetic properties associated with it. The origin of these properties lies in the electrons. Each electron in an atom behaves like a tiny magnet. Its magnetic moment originates from two types of motions (i) its orbital motion around the nucleus and (ii) its spin around its own axis. Electron being a charged particle and undergoing these motions can be considered as a small loop of current which possesses a magnetic moment. Thus, each electron has a permanent spin and an orbital magnetic moment associated with it. Magnitude of this magnetic moment is very small and is measured in the unit called Bohr magneton,  $\mu_B$ . It is equal to  $9.27 \times 10^{-24} \text{ A m}^2$ .

On the basis of their magnetic properties, substances can be classified into five categories:

(i) paramagnetic (ii) diamagnetic (iii) ferromagnetic (iv) antiferromagnetic and (v) ferrimagnetic.

(i) **Paramagnetism :**

Paramagnetic substances are weakly attracted by a magnetic field. They are magnetised in a magnetic field in the same direction. They lose their magnetism in the absence of magnetic field. Paramagnetism is due to presence of one or more unpaired electrons which are attracted by the magnetic field.  $\text{O}_2$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$  are some examples of such substances.

(ii) **Diamagnetism :**

Diamagnetic substances are weakly repelled by a magnetic field.  $\text{H}_2\text{O}$ ,  $\text{NaCl}$  and  $\text{C}_6\text{H}_6$  are some examples of such substances. They are weakly magnetised in a magnetic field in opposite direction. Diamagnetism is shown by those substances in which all the electrons are paired and there are no unpaired electrons. Pairing of electrons cancels their magnetic moments and they lose their magnetic character.

(iii) **Ferromagnetism :**

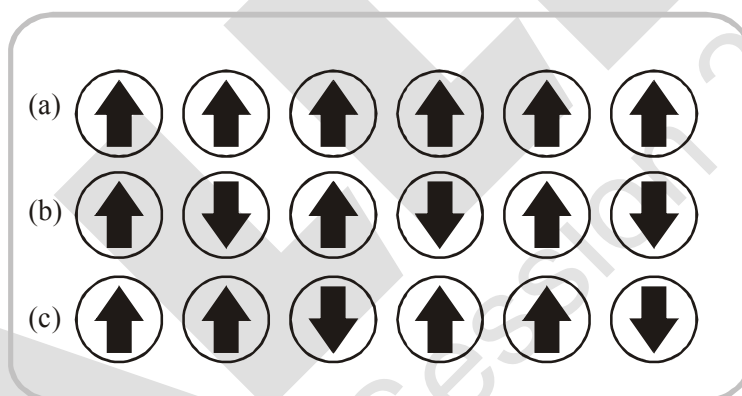
A few substances like iron, cobalt, nickel, gadolinium and  $\text{CrO}_2$  are attracted very strongly by a magnetic field. Such substances are called ferromagnetic substances. Besides strong attractions, these substances can be permanently magnetised. In solid state, the metal ions of ferromagnetic substances are grouped together into small regions called **domains**. Thus, each domain acts as a tiny magnet. In an unmagnetised piece of a ferromagnetic substance the domains are randomly oriented and their magnetic moments get cancelled. When the substance is placed in a magnetic field all the domains get oriented in the direction of the magnetic field and a strong magnetic effect is produced. This ordering of domains persists even when the magnetic field is removed and the ferromagnetic substance becomes a permanent magnet.

(iv) **Antiferromagnetism :**

Substances like  $\text{MnO}$  showing antiferromagnetism have domain structure similar to ferromagnetic substance, but their domains are oppositely oriented and cancel out each other's magnetic moment

(v) **Ferrimagnetism :**

Ferrimagnetism is observed when the magnetic moments of the domains in the substance are aligned in parallel and anti-parallel directions in unequal numbers. They are weakly attracted by magnetic field as compared to ferromagnetic substances.  $\text{Fe}_3\text{O}_4$  (magnetite) and ferrites like  $\text{MgFe}_2\text{O}_4$  and  $\text{ZnFe}_2\text{O}_4$  are examples of such substances. These substances also lose ferrimagnetism on heating and become paramagnetic.



Schematic alignment of magnetic moments in (a) ferromagnetic  
(b) antiferromagnetic and (c) ferrimagnetic

## EXERCISE # S-I

## METALLIC CRYSTALS

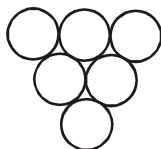
## Cubic crystals

1. A closed packed structure of uniform spheres has the edge length of 600 pm. Calculate the radius of sphere, if it exist in ( $\sqrt{2} = 1.4, \sqrt{3} = 1.7$ )  
(a) simple cubic lattice (b) BCC lattice (c) FCC lattice
2. Xenon crystallises in the face-centred cubic lattice and the edge length of the unit cell is  $438\sqrt{2}$  pm. What is the nearest neighbour distance and what is the radius of xenon atom?
3. The effective radius of the iron atom is  $\sqrt{2}$  Å. It has FCC structure. Calculate its density ( $\text{Fe} = 56 \text{ amu}$ ,  $N_A = 6 \times 10^{23}$ )
4. Calculate the ratio of densities if same element undergoes fcc as well as simple cubic packing. Assume same atomic radius in both crystals.
5. Potassium has body-centred cubic structure with the nearest neighbour distance  $260\sqrt{3}$  pm. Its density would be ( $\frac{1}{(5.2)^2} = 0.036$ ,  $N_A = 6 \times 10^{23}$ ,  $K = 39$ )
6. A cubic solid is made up of two elements 'A' and 'B'. Atoms 'B' are at the corners of the cube and 'A' at the body centre. What is the simplest formula of compound?
7. An element 'X' crystallizes in bcc. Find volume of unit cell in  $(\text{Å})^3$ , if atomic radius is  $\sqrt{3}$  Å.
8. A lattice has simple cube unit cell then number of faces which meets at a corner of a cube in this lattice is.
9. How many next nearest neighbours does potassium have in bcc lattice?
10. Number of crystal systems having, only 2 types of Bravais lattices = x,  
Number of crystal systems having, atleast 2 interfacial angles equal = y,  
all the three interfacial angles and all the three axes lengths equal = z  
Then find  $y - (x + z)$ .

## PACKING IN SOLIDS

11. A cubic solid is made by atoms 'A' forming close pack arrangement, 'B' occupying one-fourth of tetrahedral void and C occupying half of the octahedral voids. What is the formula of compound?
12. If number of nearest neighbours, next nearest ( $2^{\text{nd}}$  nearest) neighbour and next to next nearest ( $3^{\text{rd}}$  nearest) neighbours are x, y and z respectively for body centred cubic unit cell, then calculate value of  $\frac{xy}{z}$  is.
13. In FCC unit cell, what fraction of edge is not covered by atoms?
14. Element A crystallizes in hcp. Calculate total number of tetrahedral voids in 24 micrograms of A ( $N_A = 6 \times 10^{23}$ , Atomic mass of A = 48)
15. For ABC ABC ABC .... packing, distance between two successive tetrahedral void is X and distance between two successive octahedral void is y in an unit cell, then  $\frac{y\sqrt{2}}{X}$  is

16. An element 'M' crystallizes in ABAB....type packing. If adjacent layer A & B are  $10 \frac{\sqrt{2}}{\sqrt{3}}$  pm apart, then calculate radius of largest sphere which can be fitted in the void without disturbing the lattice arrangement (Given :  $\sqrt{2} = 1.414$ )
17. A 3d unit cell is such that one of its planes has the following arrangement of atoms.



What will be the number of next nearest neighbour in such unit cell?

18. The density of solid Argon is 1.6 gm/ml at  $-233^\circ\text{C}$ . If the atomic volume of Argon is assumed to be  $\frac{5}{3} \times 10^{-23} \text{ cm}^3$  then what % of solid Argon is apparently empty space ? ( $\text{Ar} = 40$ ,  $N_A = 6 \times 10^{23}$ )
19. An element crystallizes in a structure having FCC unit cell of an edge 200 pm. Calculate the density, if 200 g of this element contains  $2.4 \times 10^{24}$  atoms. ( $N_A = 6 \times 10^{23}$ )
20. Find packing fraction of three dimensional unit cell of AAAAAA.....type hypothetical arrangement in which hexagonal packing is taken in layer.

### IONIC CRYSTALS

21. If the radius of  $\text{Mg}^{2+}$  ion,  $\text{Cs}^+$  ion,  $\text{O}^{2-}$  ion,  $\text{S}^{2-}$  ion and  $\text{Cl}^-$  ion are 0.65 Å, 1.69 Å, 1.40 Å, 1.84 Å, and 1.81 Å respectively, calculate the co-ordination numbers of the cations in the crystals of MgS, MgO and CsCl.
22. The two ions  $\text{A}^+$  and  $\text{B}^-$  have radii 88 pm and 200 pm respectively. In the closed packed crystal of compound AB, predict the co-ordination number of  $\text{A}^+$ .
23. Spinel is a important class of oxides consisting of two types of metal ions with the oxide ions arranged in CCP pattern. The normal spinel has one-eight of the tetrahedral holes occupied by one type of metal ion and one half of the octahedral hole occupied by another type of metal ion. Such a spinel is formed by  $\text{Zn}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{O}^{2-}$ , with  $\text{Zn}^{2+}$  in the tetrahedral holes. Give the formula of spinel.
24. KF crystallizes in the NaCl type structure. If the radius of  $\text{K}^+$  ion is 132 pm and that of  $\text{F}^-$  ion is 135 pm, what is the shortest K–F distance? What is the edge length of the unit cell? What is the closet  $\text{K}^+ - \text{K}^+$  distance?
25. CsCl has bcc unit cell with edge length 400 pm. Calculate the interionic distance in CsCl.
26. The density of KBr is  $2.38 \text{ g cm}^{-3}$ . The length of the edge of the unit cell is 700 pm. Find the number of formula unit of KBr present in the single unit cell.  
( $N_A = 6 \times 10^{23} \text{ mol}^{-1}$ , At. mass : K = 39, Br = 80)
27. A crystal of lead(II) sulphide has NaCl structure. In this crystal the shortest distance between  $\text{Pb}^{+2}$  ion and  $\text{S}^{2-}$  ion is 300 pm. What is the length of the edge of the unit cell in lead sulphide? Also calculate the unit cell volume.

28. If the length of the body diagonal for CsCl which crystallises into a cubic structure with  $\text{Cl}^-$  ions at the corners and  $\text{Cs}^+$  ions at the centre of the unit cell, is 7 Å and the radius of the  $\text{Cs}^+$  ion is 1.69 Å, what is the radius of  $\text{Cl}^-$  ion?
29. RbI crystallizes in (8 : 8) structure in which each  $\text{Rb}^+$  is surrounded by eight iodide ions each of radius 2.17 Å. Find the length of one side of RbI unit cell, assuming anion, anion contact.
30. Solid AB has NaCl type structure. If the radius of  $\text{A}^+$  and  $\text{B}^-$  are 0.8 Å and 1.2 Å respectively and formula mass of AB is 48 g/mole, what is the density of AB solid.

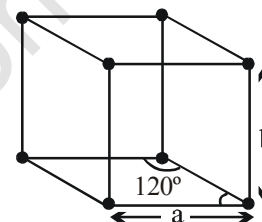
Take : Avogadro's number =  $6 \times 10^{23}$

#### PROBLEMS RELATED WITH DEFECTS IN SOLID

31. The composition of a sample of wustite is  $\text{Fe}_{0.93}\text{O}_{1.0}$ . What percentage of iron is present in the form of Fe(III)?
32. If NaCl is doped with  $10^{-3}$  mol %  $\text{SrCl}_2$ , what is the number of cation vacancies per mole of NaCl? ( $N_A = 6 \times 10^{23}$ )
33. AgCl has the same structure as that of NaCl. The edge length of unit cell of AgCl is found to be 523.5 pm and the density of AgCl is  $6.0 \text{ g cm}^{-3}$ . Find the percentage of sites that are unoccupied.  
[Ag = 108,  $(5.235)^3 = 143.5$ ]
34. A non stoichiometric compound  $\text{Fe}_7\text{S}_8$  consist of iron in both  $\text{Fe}^{+2}$  and  $\text{Fe}^{+3}$  form and sulphur is present as sulphide ions. Calculate cation vacancies as a percentage of  $\text{Fe}^{+2}$  initially present in the ideal crystal.
35. The density of ZnS crystal (Zinc blende structure) having 10% Frenkel defect is  
[  $r_{\text{Zn}^{2+}} = 40\sqrt{3}\text{pm}$ ,  $r_{\text{S}^{2-}} = 110\sqrt{3}\text{pm}$ , Zn = 65.2, S = 32 ]

EXERCISE # S-II

- An element (atomic weight = 125) crystallises in simple cubic structure. Diameter of the largest atom which can be placed without disturbing unit cell is 366 pm. If the density of element 'x'  $\text{gm/cm}^3$ , the value of  $\left(\frac{6x}{5}\right)$  is. [Given :  $\sqrt{3} = 1.732$ ,  $N_A = 6 \times 10^{23}$ ]
- The density of diamond from the fact that it has face centred cubic structure with two atoms per lattice point and unit cell edge length of 3.6 Å, is 'x'  $\text{gm/cm}^3$ , then the value of  $(1.458x)$  is ( $N_A = 6 \times 10^{23}$ )
- Iron crystallizes in several modifications. At about  $910^\circ\text{C}$ , the body-centred cubic ' $\alpha$ ' form undergoes a transition to the face-centred cubic ' $\gamma$ ' form. Assuming that the distance between nearest neighbours is the same in the two forms at the transition temperature, the ratio of the density of  $\gamma$  iron to that of  $\alpha$  iron at the transition temperature,  $x : 1$ , then the value of  $(3\sqrt{6}x)$  is.
- What is the percent by mass of titanium in rutile, a mineral that contain titanium and oxygen, if structure can be described as a closest packed array of oxide ions, with titanium in one half of the octahedral holes. What is the oxidation number of titanium? (Ti = 48)
- An element crystallizes into a structure which may be described by a cubic type of unit cell having one atom on each corner of the cube and two extra atoms on one of its body diagonal. If the volume of this unit cell is  $2.4 \times 10^{-23} \text{ cm}^3$  and density of element is  $7.2 \text{ g cm}^{-3}$ , calculate the number of atoms present in 288 g of element.
- What will be packing fraction of solid in which atoms are present at corners and cubic void is occupied. The insertion of the sphere into void does not disturb simple cubic lattice.
- Ice crystallizes in a hexagonal lattice. At the low temperature at which the structure was determined, the lattice constants where  $a = 5 \text{ Å}$ , and  $b = 3.5\sqrt{3} \text{ Å}$   
How many molecules are contained in the given unit cell?  
[density (ice) =  $\frac{16}{17.5} \text{ gm/cm}^3$ ]
- The mineral hawleyite, one form of CdS, crystallizes in one of the cubic lattices, with edge length  $5.87 \text{ Å}$ . The density of hawleyite is  $4.63 \text{ g cm}^{-3}$ . (Cd = 112)  
(i) In which cubic lattice does hawleyite crystallize?  
(ii) Find the Schottky defect in  $\text{g cm}^{-3}$ .
- KCl crystallizes in the same type of lattice as does NaCl. Given that  $\frac{r_{\text{Na}^+}}{r_{\text{Cl}^-}} = 0.5$  and  $\frac{r_{\text{Na}^+}}{r_{\text{K}^+}} = 0.7$   
Calculate :  
(a) The ratio of the sides of unit cell for KCl to that for NaCl and  
(b) The ratio of densities of NaCl to that for KCl.



$$\left(\left(\frac{8}{7}\right)^3 = 1.5, \frac{74.5}{58.5} = 1.25\right)$$

10. A cubic unit cell contains manganese ions at the corners and fluoride ions at the center of each edge.
- What is the empirical formula of the compound?
  - What is the co-ordination number of the Mn ion?
  - Calculate the edge length of the unit cell, if the radius of Mn ion is  $0.65 \text{ \AA}$  and that of  $\text{F}^-$  ion is  $1.36 \text{ \AA}$ .
11. Potassium crystallizes in a body-centred cubic lattice with edge length,  $a = 5.2 \text{ \AA}$ .
- What is the distance between nearest neighbours?
  - What is the distance between next-nearest neighbours?
  - How many nearest neighbours does each K atom have?
  - How many next-nearest neighbours does each K atom have?
  - What is the density of crystalline potassium?
- (Given :  $K = 39$ ,  $(5.2)^3 = 140$ )
12. An element X (atomic weight =  $24 \text{ gm/mole}$ ) forms a face centred cubic lattice. If the edge length of the lattice is  $4 \times 10^{-8} \text{ cm}$  and the observed density is  $2.40 \times 10^3 \text{ kg/m}^3$ , calculate the percentage occupancy of lattice points by X element. (Given :  $N_A = 6 \times 10^{23}$ )
13. Calculate the density (in  $\text{gm/cm}^3$ ) of NaCl type ionic solid ( $\text{MW} = 75 \text{ gm/mol}$ ) if distance between two nearest cations is  $250\sqrt{2} \text{ pm}$  (avogadro number =  $6 \times 10^{23}$ )
14. The olivine series of minerals consists of crystals in which Fe and Mg ions may substitute for each other causing substitutional impurity defect without changing the volume of the unit cell. In olivine series of minerals, oxide ion exist as FCC with  $\text{Si}^{4+}$  occupying  $1/4$  th of octahedral voids and divalent ions occupying  $1/4$ th of tetrahedral voids. The density of forsterite (magnesium silicate) is  $3.0 \text{ g/cc}$  and that of fayalite (ferrous silicate) is  $4.0 \text{ g/cc}$ . Find the formula of forsterite and fayalite minerals and the mass percentage of fayalite in an olivine with a density of  $3.5 \text{ g/cc}$ .



## EXERCISE # O-I

## SINGLE CORRECT :

- Which of the following are the correct axial distances and axial angles for rhombohedral system ?  
 (A)  $a = b = c, \alpha = \beta = \gamma \neq 90^\circ$  (B)  $a = b \neq c, \alpha = \beta = \gamma = 90^\circ$   
 (C)  $a \neq b = c, \alpha = \beta = \gamma = 90^\circ$  (D)  $a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$
- $a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$  represents  
 (A) tetragonal system (B) orthorhombic system  
 (C) monoclinic system (D) triclinic system
- Diamond belongs to the crystal system :  
 (A) Cubic (B) triclinic (C) tetragonal (D) hexagonal
- A match box exhibits -  
 (A) Cubic geometry (B) Monoclinic geometry  
 (C) Tetragonal geometry (D) Orthorhombic geometry
- Which of the following solids substances will have same refractive index when measured in different directions?  
 (A) NaCl (B) Monoclinic sulphur (C) Rubber (D) Graphite
- In the body-centred cubic unit cell & face centred cubic unit cell, the radius of atom in terms of edge length(a) of the unit cell is respectively:  
 (A)  $\frac{a}{2}, \frac{a}{2\sqrt{2}}$  (B)  $\frac{a}{2\sqrt{2}}, \frac{\sqrt{3}a}{4}$  (C)  $\frac{\sqrt{3}a}{4}, \frac{a}{2\sqrt{2}}$  (D)  $\frac{\sqrt{3}a}{2}, \frac{a}{2\sqrt{2}}$
- Crystal system in which maximum number of Bravais lattices are possible is  
 (A) Cubic (B) Triclinic (C) Orthorhombic (D) Rhombohedral
- Number of atoms at second nearest position from a given atom in a BCC structure is  
 (A) 8 (B) 6 (C) 12 (D) 4
- Percentage area of each face covered by atoms in a FCC unit cell is -  
 (A) 60.4% (B) 68% (C) 74% (D) 78.5%
- Correct sequence of the coordination number in SC, FCC & BCC is-  
 (A) 6, 8, 12 (B) 6, 12, 8 (C) 8, 12, 6 (D) 8, 6, 12
- If 'Z' is the number of atoms in the unit cell that represents the closest packing sequence ---A B C A B C ---, the number of tetrahedral voids in the unit cell is equal to  
 (A) Z (B) 2Z (C) Z/2 (D) Z/4
- The interstitial hole is called tetrahedral because  
 (A) It is formed by four spheres.  
 (B) Partly same and partly different.  
 (C) It is formed by four spheres the centres of which form a regular tetrahedron.  
 (D) None of the above three.
- The size of an octahedral void formed in a closest packed lattice as compared to tetrahedral void is  
 (A) Equal (B) Smaller (C) Larger (D) Not definite

14. If the anions (A) form hexagonal closest packing and cations (C) occupy only  $2/3$  octahedral voids in it, then the general formula of the compound is  
 (A) CA (B)  $CA_2$  (C)  $C_2A_3$  (D)  $C_3A_2$
15. Which one of the following schemes of ordering closest packed sheets of equal sized spheres do not generate close packed lattice.  
 (A) ABCABC (B) ABACABAC (C) ABBAABBA (D) ABCBCABCBC
16. Copper metal crystallizes in FCC lattice. Edge length of unit cell is 362 pm. The radius of largest atom that can fit into the voids of copper lattice without disturbing it is  
 (A) 53 pm (B) 45 pm (C) 93 pm (D) 87 pm
17. Packing fraction in 2-D hexagonal arrangement of identical sphere is  
 (A)  $\frac{\pi}{3\sqrt{2}}$  (B)  $\frac{\pi}{3\sqrt{3}}$  (C)  $\frac{\pi}{2\sqrt{3}}$  (D)  $\pi/6$
18. In fcc unit cell smallest distance between octahedral void & tetrahedral void is -  
 (a = edge length of unit cell )  
 (A)  $\frac{a}{\sqrt{2}}$  (B)  $\frac{\sqrt{3}a}{2}$  (C) a (D)  $\frac{\sqrt{3}a}{4}$
19. What is not true regarding hexagonal close packing (hcp)  
 (A) packing fraction is 0.74  
 (B) coordination number is 12  
 (C) ABC ABC.....type packing  
 (D) Containing both tetrahedral and octahedral voids
20. In which of the following arrangement distance between two nearest neighbours is maximum, considering identical sized atoms in all arrangements ?  
 (A) Simple cubic (B) bcc (C) fcc (D) equal in all
21. How many unit cell are there in 1 gram cubic crystal of NaCl ?  
 (A)  $\frac{4 \times N_A}{58.5}$  (B)  $\frac{N_A}{58.5}$  (C)  $\frac{N_A}{58.5 \times 4}$  (D)  $\frac{N_A}{58.5 \times 8}$
22. The density of  $CaF_2$  (fluorite structure) is  $3.18 \text{ g/cm}^3$ . The length of the side of the unit cell is (Ca = 40, F = 19)  
 (A) 253 pm (B) 344 pm (C) 546 pm (D) 273 pm
23. The coordination number of cation and anion in Fluorite  $CaF_2$  and CsCl are respectively  
 (A) 8:4 and 6:3 (B) 6:3 and 4:4 (C) 8:4 and 8:8 (D) 4:2 and 2:4
24. A compound XY crystallizes in 8 : 8 lattice with unit cell edge length of 480 pm. If the radius of  $Y^-$  is 225 pm, then the radius of  $X^+$  is  
 (A) 127.5 pm (B) 190.68 pm (C) 225 pm (D) 255 pm
25. The mass of a unit cell of CsCl corresponds to  
 (A) 1  $Cs^+$  and 1  $Cl^-$  (B) 1  $Cs^+$  and 6  $Cl^-$  (C) 4  $Cs^+$  and 4  $Cl^-$  (D) 8  $Cs^+$  and 1  $Cl^-$

26. An ionic compound AB has ZnS type structure. If the radius  $A^+$  is 22.5 pm, then the ideal radius of  $B^-$  would be  
 (A) 54.35 pm (B) 100 pm (C) 145.16 pm (D) none of these
27. Edge length of  $M^+X^-$  (NaCl structure) is 7.2 Å. Assuming  $M^+ - X^-$  contact along the cell edge, radius of  $X^-$  ion is ( $r_{M^+} = 1.6 \text{ Å}$ ) :  
 (A) 2.0 Å (B) 5.6 Å (C) 2.8 Å (D) 38 Å
28.  $NH_4Cl$  crystallizes in CsCl type lattice with a unit cell edge length of 387 pm. The distance between the oppositely charged ions in the lattice is  
 (A) 335.1 pm (B) 83.77 pm (C) 274.46 pm (D) 137.23 pm
29.  $r_{Na^+} = 95 \text{ pm}$  and  $r_{Cl^-} = 181 \text{ pm}$  in NaCl (rock salt) structure. What is the shortest distance between  $Na^+$  ions?  
 (A) 778.3 pm (B) 276 pm (C) 195.7 pm (D) 390.3 pm
30. AB crystallises itself as NaCl crystal. If  $r_+ = \frac{2}{\sqrt{6}}$  and  $r_- = \sqrt{6}$ , the edge length of cube is  
 (A)  $2\sqrt{3}$  (B)  $\frac{4}{\sqrt{3}}$  (C)  $\frac{8}{\sqrt{6}}$  (D)  $\frac{16}{\sqrt{6}}$
31. Which of the following is the most likely to show schottky defect ?  
 (A)  $CaF_2$  (B) ZnS (C) AgCl (D) CsCl
32. In the Schottky defect, in AB type ionic solids  
 (A) cations are missing from the lattice sites and occupy the interstitial sites  
 (B) equal number of cations and anions are missing  
 (C) anions are missing and electrons are present in their place  
 (D) equal number of extra cations and electrons are present in the interstitial sites
33. Choose the correct option.  
 (A) Two adjacent face centre atom doesn't touch each other in fcc unit cell because they are not nearest atom of face each other in fcc lattice  
 (B) Number of nearest  $Na^+$  ions of another  $Na^+$  in  $Na_2O$  crystal will be 24.  
 (C) Minimum distance between two cubical voids in simple cube unit cell lattice will be 'a' where 'a' is length of edge of unit cell  
 (D) By defects in solids, density of solids either remains constant or decreases but it can never increase.
34. The measured density of AgI is  $6.94 \text{ g/cm}^3$  and the theoretical density is  $5.67 \text{ g/cm}^3$ . These data indicate that solid AgI has -  
 (A) Schottky defect (B) Frenkel defect  
 (C) Interstitial impurities defect (D) Both (1) and (2)
35. Which of the following statement is **CORRECT** ?  
 (A) A metal can show only non- stoichiometric defects  
 (B) Schottky defect reduces the density of a solid due to significant increase in volume.  
 (C) Impurity defect always change the density.  
 (D) Solids having F-centres may have metal excess defect due to missing anions.

## EXERCISE # O-II

## SINGLE CORRECT :

- The only incorrect statement for the packing of identical spheres in two dimension is :
  - For square close packing , coordination number is 4.
  - For hexagonal close packing, coordination number is 6.
  - There is only one void per atom in both, square and hexagonal close packing.
  - Hexagonal close packing is more efficiently packed than square close packing.
- Correct statement for ccp is :
  - Each octahedral void is surrounded by 6 spheres and each sphere is surrounded by 4 octahedral voids
  - Each octahedral void is surrounded by 6 spheres and each sphere is surrounded by 6 octahedral voids
  - Each octahedral void is surrounded by 6 spheres and each sphere is surrounded by 8 octahedral voids
  - Each octahedral void is surrounded by 6 spheres and each sphere is surrounded by 12 octahedral voids
- Which of the following statements is correct in the rock-salt structure of an ionic compounds?
  - coordination number of cation is four whereas that of anion is six.
  - coordination number of cation is six whereas that of anion is four.
  - coordination number of each cation and anion is four.
  - coordination number of each cation and anion is six.

## MORE THAN ONE MAY BE CORRECT :

- Which of the following statements is/are correct :
  - In an anti-fluorite structure, anions form FCC lattice and cations occupy all tetrahedral voids.
  - If the radius of cations and anions are  $0.2 \text{ \AA}$  and  $0.95 \text{ \AA}$  , then coordination number of cation in the crystal is 4.
  - Each sphere is surrounded by six voids in two dimensional hexagonal close packed layer.
  - 8  $\text{Cs}^+$  ions occupy the second nearest neighbour locations of a  $\text{Cs}^+$  ion in  $\text{CsCl}$  crystals.
- Select correct statement(s)
  - Density of crystal always increases due to substitutional impurity defect.
  - An ion is transferred from a lattice site to an interstitial position in Frenkel defect.
  - In  $\text{AgCl}$ , the silver ion is displaced from its lattice position to an interstitial position. Such a defect is called a frenkel defect
  - None
- Lead metal has a density of  $11.34 \text{ g/cm}^3$  and crystallizes in a face-centred lattice. Choose the correct alternatives ( $\text{Pb} = 208$  ,  $N_A = 6 \times 10^{23}$ )
  - the volume of one unit cell is  $1.22 \times 10^{-22} \text{ cm}^3$ .
  - the volume of one unit cell is  $1.22 \times 10^{-19} \text{ cm}^3$ .
  - the atomic radius of lead is  $175 \text{ pm}$ .
  - the atomic radius of lead is  $155.1 \text{ pm}$ .

7. Which of the following statement(s) is/are correct ?
- (A) NaCl is a 'AB' crystal lattice that can be interpreted to be made up of two individual fcc unit cells of  $A^+$  and  $B^-$  fused together in such a manner that the corner of one unit cell becomes the edge centre of the other.
- (B) In a face centred cubic unit cell, the body centre is an octahedral void.
- (C) In fcc unit cell, octahedral and tetrahedral voids are equal in number.
- (D) Tetrahedral voids =  $2 \times$  octahedral voids, is valid for ccp and hcp.
8. Select the correct statement (s) :
- (A) CsCl mainly shows Schottky defect (B) ZnS mainly shows Frenkel defect
- (C) NaCl unit cell contain  $4Na^+$  and  $4Cl^-$  (D) Truncated octahedron have 24 corners.
9. Select the correct statement(s) –
- (A) The ionic crystal of AgBr has Schottky defect.
- (B) The unit cell having crystal parameters,  $a = b \neq c$ ,  $\alpha = \beta = 90^\circ$ ,  $\gamma = 120^\circ$  is hexagonal
- (C) Ionic compounds having Frenkel defect has high  $r^+/r^-$  ratio.
- (D) The co-ordination number of  $Na^+$  ion in NaCl is 6
10. Which of the following is/are true ?
- (A) Ratio of nearest neighbours in simple cubic cell to next nearest neighbours in face centred cubic cell is 1.
- (B) Packing efficiency of a unit cell in which atoms are present at each corner and each edge centre is about 26 % in metallic crystal.
- (C) Distance between two planes in FCC or HCP arrangement is same for a metal existing in both forms, with same atomic radius.
- (D) If number of unit cell along one edge are 'x', then total number of unit cell in cube =  $x^3$

#### ASSERTION / REASON :

11. **Statement-1** : In Antifluorite structure ( $Li_2O$ ), the oxide ions occupy c.c.p. (cubic close packing) and  $Li^+$  ions, 100% tetrahedral voids.

**Statement-2** : The distance of the nearest neighbours in antifluorite structure is  $\frac{\sqrt{3}a}{4}$ , where 'a' is the edge length of the cube

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
- (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
- (C) Statement-1 is true, statement-2 is false.
- (D) Statement-1 is false, statement-2 is true.
12. **Statement-1** : In FCC unit cell, packing efficiency is more when all tetrahedral voids are filled with spheres of maximum possible size as compared with packing efficiency when all octahedral voids are filled in similar way.
- Statement-2** : Tetrahedral voids are more in the number than octahedral voids in FCC.
- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
- (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
- (C) Statement-1 is true, statement-2 is false.
- (D) Statement-1 is false, statement-2 is true.

13. **Statement-1** : In diamond, carbon atoms occupy alternate tetrahedral voids in the FCC lattice formed by the carbon atoms.  
**Statement-2** : In diamond, packing fraction is more than 74%.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.
14. **Statement-1** : Due to Frenkel defect, there is no effect on the density of the crystalline solid.  
**Statement-2** : In Frenkel defect, no cation or anion leaves the crystal.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.
15. **Statement-1** : Conductivity of silicon increased by doping it with group 15 element.  
**Statement-2** : Doping means introduction of small amount of impurities like P or As into pure silicon crystal.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

**COMPREHENSION :****Paragraph for Q.16 & Q.17**

Solid balls of radius 17.32 cm crystallises in bcc pattern. During one such crystallisation, some oxygen gas is trapped. This trapped oxygen at 640K creates pressure of 5 atm.

**Assume :**

- (i) BCC arrangement is not disturbed due to trapping of gas.  
 (ii) Gas is uniformly distributed inside unit cell

[Take  $R = 0.08 \text{ atm-litre/mole-K}$ ,  $N_A = 6 \times 10^{23}$ , Mass of a solid ball = 64 gms]

16. Number of oxygen molecules present in an unit cell is -  
 (A)  $2.4 \times 10^{24}$  (B)  $1.2 \times 10^{24}$  (C)  $6 \times 10^{23}$  (D)  $3 \times 10^{23}$
17. Calculate percentage increase in density due to trapping of gas  
 (A) 16.67 % (B) 33.33 % (C) 100% (D) 50%

**Paragraph for Q.18 to Q.21**

Calcium crystallizes in a cubic unit cell with density 3.2 g/cc. Edge-length of the unit cell is 437 pm.

18. The type of unit cell is  
 (A) Simple cubic (B) BCC (C) FCC (D) Edge-centred
19. The nearest neighbour distance is  
 (A) 154.5 pm (B) 309 pm (C) 218.5 pm (D) 260 pm
20. The number of nearest neighbours of a Ca atom are  
 (A) 4 (B) 6 (C) 8 (D) 12

21. If the metal is melted, density of the molten metal was found to be 3 g/cc. What will be the percentage of empty space in the molten metal?
- (A) 31%                      (B) 36%                      (C) 28%                      (D) 49%

**TABLE TYPE COMPREHENSION :**

| Column-I                                  | Column-II                                      | Column-III                                   |
|-------------------------------------------|------------------------------------------------|----------------------------------------------|
| (A) NaCl (Rock salt) structure            | (i) Cation - FCC<br>Anion - Tetrahedral void   | (I) All tetrahedral voids are occupied       |
| (B) CsCl structure                        | (ii) Anion - FCC<br>Cation - Tetrahedral voids | (II) All octahedral voids are occupied       |
| (C) ZnS (zinc blende) structure           | (iii) Anion - SC<br>Cation - Cubic voids       | (III) 50 % of tetrahedral voids are occupied |
| (D) CaF <sub>2</sub> (fluorite) structure | (iv) Anion - FCC<br>Cation - Octahedral void   | (IV) All octahedral voids are empty          |

- 22.** Which of the following is correct match ?  
 (A) A, i, I (B) A, ii, IV (C) A, iv, II (D) A, iv, IV
- 23.** Which of the following is incorrect match ?  
 (A) B, iii, I (B) C, ii, III (C) D, i, I (D) D, i, IV
- 24.** Which of the following is correct match ?  
 (A) D, ii, I (B) B, iv, IV (C) D, iii, I (D) C, ii, IV

**MATCH THE COLUMN :**

- 25.** Match the column

| <b>Column I</b>              | <b>Column II</b>            |
|------------------------------|-----------------------------|
| (A) Tetragonal and Hexagonal | (P) are two crystal systems |
| (B) Cubic and Rhombohedral   | (Q) $a = b \neq c$          |
| (C) Monoclinic and Triclinic | (R) $a \neq b \neq c$       |
| (D) Cubic and Hexagonal      | (S) $a = b = c$             |

- 26.** Match the column:

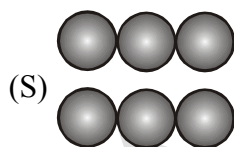
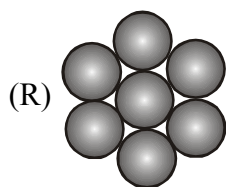
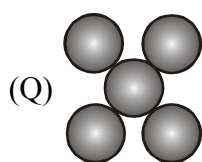
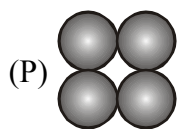
| <b>Column I</b>          | <b>Column II</b>                                               |
|--------------------------|----------------------------------------------------------------|
| (A) Rock salt structure  | (P) Co-ordination number of cation is 4                        |
| (B) Zinc Blend structure | (Q) $\frac{\sqrt{3}a}{4} = r_+ + r_-$                          |
| (C) Fluorite structure   | (R) Co-ordination number of cation and anion are same          |
|                          | (S) Distance between two nearest anion is $\frac{a}{\sqrt{2}}$ |

## MATCHING LIST TYPE :

27. Match the column

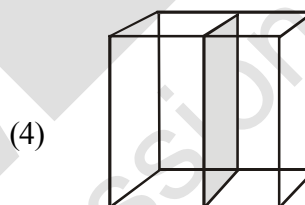
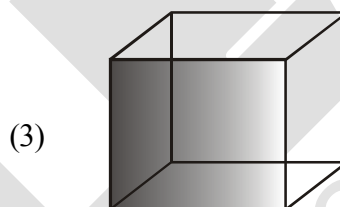
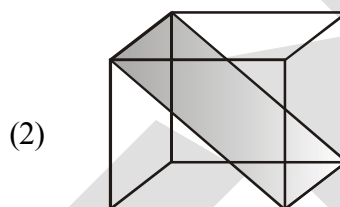
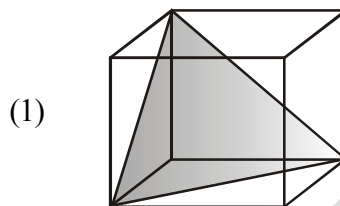
## Column I

(Arrangement of the atoms/ions)



## Column II

(Planes in fcc lattice)



Code:

|     | P | Q | R | S |
|-----|---|---|---|---|
| (A) | 4 | 3 | 1 | 2 |
| (B) | 4 | 3 | 2 | 1 |
| (C) | 3 | 2 | 1 | 4 |
| (D) | 1 | 2 | 4 | 3 |



28. Column I

Column II

[Distance in terms of edge length of cube (a)]

(P) 0.866 a

(1) Shortest distance between cation & anion in CsCl structure.

(Q) 0.707 a

(2) Shortest distance between two cation in  $\text{CaF}_2$  structure.

(R) 0.433 a

(3) Shortest distance between carbon atoms in diamond.

(S) a

(4) shortest distance between next nearest cations in rock salt structure.

Code:

|     | P | Q | R | S |
|-----|---|---|---|---|
| (A) | 4 | 3 | 1 | 2 |
| (B) | 1 | 2 | 3 | 4 |
| (C) | 3 | 2 | 1 | 4 |
| (D) | 1 | 2 | 4 | 3 |

## EXERCISE # J-MAIN

- The no. of atoms per unit cell in B.C.C. & F.C.C. is respectively : [AIEEE-02]  
 (1) 8, 10 (2) 2, 4 (3) 1, 2 (4) 1, 3
- How many unit cells are present in a cube-shaped ideal crystal of NaCl of mass 1.00g ? [AIEEE-03]  
 (1)  $1.28 \times 10^{21}$  unit cells (2)  $1.71 \times 10^{21}$  unit cells  
 (3)  $2.57 \times 10^{21}$  unit cells (4)  $5.14 \times 10^{21}$  unit cells
- What type of crystal defect is indicated in the diagram below ? [AIEEE-04]  

|                 |                 |                 |                 |                 |                 |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Na <sup>+</sup> | Cl <sup>-</sup> | Na <sup>+</sup> | Cl <sup>-</sup> | Na <sup>+</sup> | Cl <sup>-</sup> |
| Cl <sup>-</sup> |                 | Cl <sup>-</sup> | Na <sup>+</sup> |                 | Na <sup>+</sup> |
| Na <sup>+</sup> | Cl <sup>-</sup> |                 | Cl <sup>-</sup> | Na <sup>+</sup> | Cl <sup>-</sup> |
| Cl <sup>-</sup> | Na <sup>+</sup> | Cl <sup>-</sup> | Na <sup>+</sup> |                 | Na <sup>+</sup> |

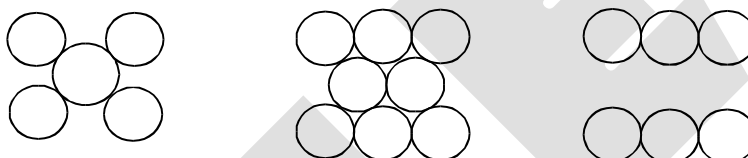
 (1) Frenkel defect (2) Schottky defect  
 (3) Interstitial defect (4) Frenkel and Schottky defects
- An ionic compound has a unit cell consisting of A ions at the corners of a cube and B ions on the centres of the faces of the cube. The empirical formula of this compound would be- [AIEEE-05]  
 (1) A<sub>2</sub>B (2) AB (3) A<sub>3</sub>B (4) AB<sub>3</sub>
- Lattice energy of an ionic compound depends upon - [AIEEE-05]  
 (1) Size of the ion only (2) Charge on the ion only  
 (3) Charge on the ion and size of the ion (4) Packing of ions only
- Total volume of atoms present in a face-centred cubic unit cell of a metal is (r is atomic radius) : [AIEEE-06]  
 (1)  $\frac{24}{3}\pi r^3$  (2)  $\frac{12}{3}\pi r^3$  (3)  $\frac{16}{3}\pi r^3$  (4)  $\frac{20}{3}\pi r^3$
- In a compound, atoms of element Y form ccp lattice and those of element X occupy  $\frac{2}{3}$ rd of tetrahedral voids. The formula of the compound will be - [AIEEE-08]  
 (1) X<sub>4</sub>Y<sub>3</sub> (2) X<sub>2</sub>Y<sub>3</sub> (3) X<sub>2</sub>Y (4) X<sub>3</sub>Y<sub>4</sub>
- The edge length of a face centred cubic cell of an ionic substance is 508 pm. If the radius of the cation is 110 pm, the radius of the anion is :- [AIEEE-10]  
 (1) 144 pm (2) 288 pm (3) 398 pm (4) 618 pm
- Percentages of free space in cubic close packed structure and in body centred packed structure are respectively :- [AIEEE-10]  
 (1) 48% and 26% (2) 30% and 26% (3) 26% and 32% (4) 32% and 48%

10. The radius of a calcium ion is 94 pm and of the oxide ion is 146 pm. The possible crystal structure of calcium oxide will be :- [Jee-Main (online)-12]  
 (1) Octahedral (2) Tetrahedral (3) Pyramidal (4) Trigonal
11. Ammonium chloride crystallizes in a body centred cubic lattice with edge length of unit cell of 390 pm. If the size of chloride ion is 180 pm, the size of ammonium ion would be: [Jee-Main (online)-12]  
 (1) 158 pm (2) 174 pm (3) 142 pm (4) 126 pm
12. A solid has 'bcc' structure. If the distance of nearest approach between two atoms is  $1.73 \text{ \AA}$ , the edge length of the cell is :- [Jee-Main (online)-12]  
 (1) 314.20 pm (2) 216 pm (3) 200 pm (4) 1.41 pm
13. Among the following the incorrect statement is :- [Jee-Main (online)-12]  
 (1) Density of crystals remains unaffected due to Frenkel defect  
 (2) In BCC unit cell the void space is 32%  
 (3) Electrical conductivity of semiconductors and metals increases with increase in temperature  
 (4) Density of crystals decreases due to Schottky defect
14. Copper crystallises in fcc with a unit cell edge length of 361 pm. What is the radius of copper atom? [AIEEE-2011]  
 (1) 181 pm (2) 128 pm (3) 157 pm (4) 108 pm
15. Lithium forms body centred cubic structure. The length of the side of its unit cell is 351 pm. Atomic radius of the lithium will be :- [Jee-Main (offline)-12]  
 (1) 152 pm (2) 75 pm (3) 300 pm (4) 240 pm
16. In a face centred cubic lattice, atoms of A form the corner points and atoms of B form the face centred points. If two atoms of A are missing from the corner points, the formula of the ionic compound is [Jee-Main (online)-13]  
 (1)  $AB_2$  (2)  $AB_3$  (3)  $AB_4$  (4)  $A_2B_5$
17. Which one of the following statements about packing in solids is **incorrect** ? [Jee-Main (online)-13]  
 (1) Void space in ccp mode of packing is 26%  
 (2) Coordination number in hcp mode of packing is 12  
 (3) Void space in hcp mode of packing is 32%  
 (4) Coordination number in bcc mode of packing is 8
18. An element having an atomic radius of 0.14 nm crystallizes in an fcc unit cell. What is the length of a side of the cell ? [Jee-Main (online)-13]  
 (1) 0.96 nm (2) 0.4 nm (3) 0.24 nm (4) 0.56 nm

19. Experimentally it was found that a metal oxide has formula  $M_{0.98}O$ . Metal M, is present as  $M^{2+}$  and  $M^{3+}$  in its oxide. Fraction of the metal which exists as  $M^{3+}$  would be :- [Jee-Main (offline)-13]  
 (1) 7.01% (2) 4.08% (3) 6.05% (4) 5.08
20. The total number of octahedral void(s) per atom present in a cubic close packed structure is :- [Jee-Main (online)-14]  
 (1) 1 (2) 2 (3) 3 (4) 4
21. In a monoclinic unit cell, the relation of sides and angles are respectively [Jee-Main (online)-14]  
 (1)  $a \neq b \neq c$  and  $\alpha \neq \beta \neq \gamma \neq 90^\circ$  (2)  $a \neq b \neq c$  and  $\beta = \gamma = 90^\circ \neq \alpha$   
 (3)  $a = b \neq c$  and  $\alpha = \beta = \gamma = 90^\circ$  (4)  $a \neq b \neq c$  and  $\alpha = \beta = \gamma = 90^\circ$
22. The appearance of colour in solid alkali metal halides is generally due to : [Jee-Main (online)-14]  
 (1) Frenkel defect (2) F-centres (3) Schottky defect (4) Interstitial position
23. In a face centred cubic lattice atoms A are at the corner points and atoms B at the face centred points. If atom B is missing from one of the face centred points, the formula of the ionic compound is : [AIEEE-2011, Jee-Main (online)-14]  
 (1)  $AB_2$  (2)  $A_2B_3$  (3)  $A_5B_2$  (4)  $A_2B_5$
24. CsCl crystallises in body centred cubic lattice. if 'a' is its edge length then which of the following expression is correct : [Jee-Main (offline)-14]  
 (1)  $r_{Cs^+} + r_{Cl^-} = \frac{\sqrt{3}}{2}a$  (2)  $r_{Cs^+} + r_{Cl^-} = \sqrt{3}a$  (3)  $r_{Cs^+} + r_{Cl^-} = 3a$  (4)  $r_{Cs^+} + r_{Cl^-} = \frac{3a}{2}$
25. Sodium metal crystallizes in a body centred cubic lattice with a unit cell edge of  $4.29 \text{ \AA}$ . The radius of sodium atom is approximately :- [Jee-Main (offline)-15]  
 (1)  $5.72 \text{ \AA}$  (2)  $0.93 \text{ \AA}$  (3)  $1.86 \text{ \AA}$  (4)  $3.022 \text{ \AA}$
26. Which of the following compounds is metallic and ferromagnetic ? [Jee-Main (offline)-16]  
 (1)  $MnO_2$  (2)  $TiO_2$  (3)  $CrO_2$  (4)  $VO_2$
27. A metal crystallises in a face centred cubic structure. If the edge length of its unit cell is 'a', the closest approach between two atoms in metallic crystal will be :- [Jee-Main (offline)-17]  
 (1)  $2a$  (2)  $2\sqrt{2}a$  (3)  $\sqrt{2}a$  (4)  $\frac{a}{\sqrt{2}}$
28. Which type of effect 'defect' has the presence of cations in the interstitial sites - [Jee-Main (offline)-18]  
 (1) Vacancy defect (2) Frenkel defect  
 (3) Metal deficiency defect (4) Schottky defect
29. All of the following share the same crystal structure except :- [Jee-Main (online)-18]  
 (1) RbCl (2) CsCl (3) LiCl (4) NaCl
30. Which of the following arrangements shows the schematic alignment of magnetic moments of antiferromagnetic substance ? [Jee-Main (online)-18]  
 (1)  $\uparrow \downarrow \downarrow \downarrow \downarrow \uparrow$  (2)  $\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow$   
 (3)  $\uparrow \uparrow \downarrow \uparrow \uparrow \downarrow$  (4)  $\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$

### ***EXERCISE #.J-ADVANCED***

1. A metal crystallises into two cubic phases, FCC and BCC whose unit cell lengths are 3.5 and 3.0 Å respectively. Calculate the ratio of densities of FCC and BCC. **[JEE-1999]**
2. The coordination number of a metal crystallising in a hcp structure is **[JEE-2000]**  
(A) 12 (B) 4 (C) 8 (D) 6
3. In any ionic solid [MX] with schottky defects, the number of positive and negative ions are same. **[T/F]** **[JEE-2000]**
4. In a solid "AB" having NaCl structure "A" atoms occupy the corners of the cubic unit cell. If all the face-centred atoms along one of the axes are removed, then the resultant stoichiometry of the solid is  
(A) AB<sub>2</sub> (B) A<sub>2</sub>B (C) A<sub>4</sub>B<sub>3</sub> (D) A<sub>3</sub>B<sub>4</sub> **[JEE-2000]**
5. The figures given below show the location of atoms in three crystallographic planes in FCC lattice. Draw the unit cell for the corresponding structure and identify these planes in your diagram.



6. A substance  $A_xB_y$  crystallises in a FCC lattice in which atoms “A” occupy each corner of the cube and atoms “B” occupy the centres of each face of the cube. Identify the correct composition of the substance  $A_xB_y$ .
- (A)  $AB_3$   
(B)  $A_4B_3$   
(C)  $A_3B$   
(D) composition cannot be specified [JEE-2002]
7. Marbles of diameter 10 mm each are to be arranged on a flat surface so that their centres lie within the area enclosed by four lines of length each 40 mm. Sketch the arrangement that will give the maximum number of marbles per unit area, that can be enclosed in this manner and deduce the expression to calculate it. [JEE 2003]
8. (i) AB crystallizes in a rock salt structure with  $A : B = 1 : 1$ . The shortest distance between A and B is  $Y^{1/3}$  nm. The formula mass of AB is 6.023 Y amu where Y is any arbitrary constant. Find the density in  $\text{kg m}^{-3}$ .  
(ii) If measured density is  $20 \text{ kg m}^{-3}$ . Identify the type of point defect. [JEE-2004]
9. Which of the following FCC structure contains cations in alternate tetrahedral voids?
- (A) NaCl                      (B) ZnS                      (C)  $\text{Na}_2\text{O}$                       (D)  $\text{CaF}_2$  [JEE 2005]

10. An element crystallises in FCC lattice having edge length 400 pm. Calculate the maximum diameter which can be placed in interstitial sites without disturbing the structure. [JEE 2005]
11. The edge length of unit cell of a metal having atomic weight 75 g/mol is 5 Å which crystallizes in cubic lattice. If the density is 2 g/cc then find the radius of metal atom. ( $N_A = 6 \times 10^{23}$ ). Give the answer in pm. [JEE 2006]
12. Match the crystal system / unit cells mentioned in Column I with their characteristic features mentioned in Column II. Indicate your answer by darkening the appropriate bubbles of the  $4 \times 4$  matrix given in the ORS.

## Column I

- (A) simple cubic and face-centred cubic
- (B) cubic and rhombohedral
- (C) cubic and tetragonal
- (D) hexagonal and monoclinic

## Column II

- (P) have these cell parameters  $a = b = c$  and  $\alpha = \beta = \gamma$
- (Q) are two crystal systems
- (R) have only two crystallographic angles of  $90^\circ$
- (S) belong to same crystal system.

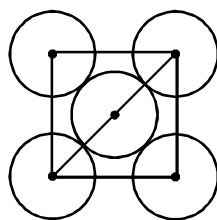
[JEE 2007]

## Paragraph for Question No.13 to 15

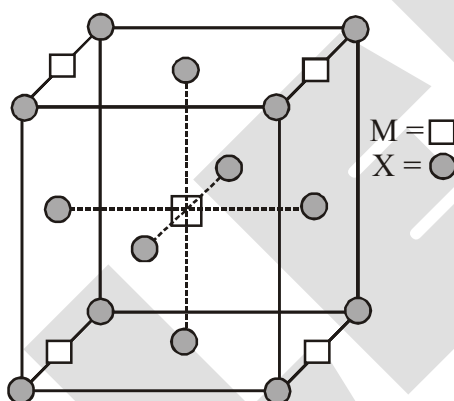
In hexagonal systems of crystals, a frequently encountered arrangement of atoms is described as a hexagonal prism. Here, the top and bottom of the cell are regular hexagons and three atoms are sandwiched in between them. A space-filling model of this structure, called hexagonal close-packed (HCP), is constituted of a sphere on a flat surface surrounded in the same plane by six identical spheres as closely as possible. Three spheres are then placed over the first layer so that they touch each other and represent the second layer. Each one of these three spheres touches three spheres of the bottom layer. Finally, the second layer is covered with a third layer that is identical to the bottom layer in relative position. Assume radius of every sphere to be 'r'.

13. The number of atoms in this HCP unit cells is [JEE 2008]  
 (A) 4 (B) 6 (C) 12 (D) 17
14. The volume of this HCP unit cell is [JEE 2008]  
 (A)  $24\sqrt{2} r^3$  (B)  $16\sqrt{2} r^3$  (C)  $12\sqrt{2} r^3$  (D)  $\frac{64}{3\sqrt{3}} r^3$
15. The empty space in this HCP unit cell is [JEE 2008]  
 (A) 74% (B) 47.6 % (C) 32% (D) 26%
16. The correct statement(s) regarding defects in solid is (are) [JEE 2009]  
 (A) Frenkel defect is usually favoured by a very small difference in the sizes of cation and anion.  
 (B) Frenkel defect is a dislocation defect  
 (C) Trapping of an electron in the lattice leads to the formation of F-center.  
 (D) Schottky defects have no effect on the physical properties of solids.

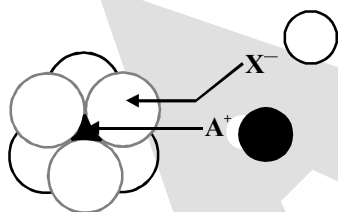
17. The packing efficiency of the two-dimensional square unit cell shown below is [JEE-2010]



- (A) 39.27% (B) 68.02% (C) 74.05% (D) 78.54%
18. The number of hexagonal faces that present in a truncated octahedron is. [JEE-2011]
19. A compound  $M_pX_q$  has cubic close packing (ccp) arrangement of X. Its unit cell structure is shown below. The empirical formula of the compound is : [JEE-2012]



- (A) MX (B)  $MX_2$  (C)  $M_2X$  (D)  $M_5X_{14}$
20. The arrangement of  $X^-$  ions around  $A^+$  ion in solid AX is given in the figure (not drawn to scale). If the radius of  $X^-$  is 250 pm, the radius of  $A^+$  is - [JEE-2013]



- (A) 104 pm (B) 125 pm (C) 183 pm (D) 57 pm
21. If the unit cell of a mineral has cubic close packed (ccp) array of oxygen atoms with m fraction of octahedral holes occupied by aluminium ions and n fraction of tetrahedral holes occupied by magnesium ions m and n respectively, are - [JEE-2015]
- (A)  $\frac{1}{2}, \frac{1}{8}$  (B)  $1, \frac{1}{4}$  (C)  $\frac{1}{2}, \frac{1}{2}$  (D)  $\frac{1}{4}, \frac{1}{8}$

22. The **CORRECT** statement(s) for cubic close packed (ccp) three dimensional structure is (are)  
(A) The number of the nearest neighbours of an atom present in the topmost layer is 12  
(B) The efficiency of atom packing is 74% [JEE-2016]  
(C) The number of octahedral and tetrahedral voids per atom are 1 and 2, respectively  
(D) The unit cell edge length is  $2\sqrt{2}$  times the radius of the atom
23. A crystalline solid of a pure substance has a face-centred cubic structure with a cell edge of 400 pm. If the density of the substance in the crystal is  $8\text{ g cm}^{-3}$ , then the number of atoms present in 256g of the crystal is  $N \times 10^{24}$ . The value of N is [JEE-2017]
24. Consider an ionic solid MX with NaCl structure. Construct a new structure (Z) whose unit cell is constructed from the unit cell of MX following the sequential instructions given below. Neglect the charge balance. [JEE-2018]  
(i) Remove all the anions (X) except the central one  
(ii) Replace all the face centered cations (M) by anions (X)  
(iii) Remove all the corner cations (M)  
(iv) Replace the central anion (X) with cation (M)

The value of  $\left(\frac{\text{number of anions}}{\text{number of cations}}\right)$  in Z is \_\_\_\_.



# ANSWER KEY

## EXERCISE # S-I

1. Ans. (a) 300 pm, (b) 255 pm, (c) 210 pm
2. Ans. 438 pm, 219 pm
3. Ans. 5.83 g cm<sup>-3</sup>
4. Ans. ( $\sqrt{2} : 1$ )
5. Ans. (0.9 gm/cm<sup>-3</sup>)
6. Ans. AB
7. Ans. (64)
8. Ans. (12)
9. Ans. (6)
10. Ans. (2)
11. Ans. A<sub>2</sub>BC
12. Ans. (4)
13. Ans. (0.293)
14. Ans. ( $6 \times 10^{17}$ )
15. Ans. (2)  $\frac{\frac{a}{\sqrt{2}} \times \sqrt{2}}{a/2} = 2$
16. Ans. (2.07 pm)
17. Ans. (6)
18. Ans. (60%)
19. Ans. 41.67 g cm<sup>-3</sup>
20. Ans. 0.60
21. Ans. 4, 6, 8
22. Ans. (6)
23. Ans. ZnAl<sub>2</sub>O<sub>4</sub>
24. Ans. 267 pm, 534 pm, 377.6 pm
25. Ans. 346.4 pm
26. Ans. 4
27. Ans. a = 600 pm, V =  $2.16 \times 10^{-22}$  cm<sup>3</sup>
28. Ans. 1.81 Å
29. Ans. 4.34 Å
30. Ans. (5 gm/cm<sup>3</sup>)
31. Ans. 15.05 %
32. Ans.  $6.0 \times 10^{18}$
33. Ans. 10
34. Ans. 12.5%
35. Ans. 3.0 gm/cm<sup>3</sup>

## EXERCISE # S-II

1. Ans. (2)
2. Ans. (5)
3. Ans. 8
4. Ans. 60%, +4
5. Ans.  $5 \times 10^{24}$
6. Ans. 0.72
7. Ans. 4
8. Ans. (i) FCC (ii) 0.116 g/cc
9. Ans. (a) 1.143, (b) 1.2
10. Ans. (a) MnF<sub>3</sub>, (b) 6, (c) 4.02 Å
11. Ans. (a) 4.5 Å, (b) 5.2 Å, (c) 8, (d) 6, (e) 0.929 g/cm<sup>3</sup>
12. Ans. 96%
13. Ans. (4)
14. Ans. Mg<sub>2</sub>SiO<sub>4</sub>, Fe<sub>2</sub>SiO<sub>4</sub>, 57.14%

**EXERCISE # O-I**

- |             |             |             |
|-------------|-------------|-------------|
| 1. Ans.(A)  | 2. Ans.(D)  | 3. Ans.(A)  |
| 4. Ans.(D)  | 5. Ans.(C)  | 6. Ans.(C)  |
| 7. Ans. (C) | 8. Ans (B)  | 9. Ans (D)  |
| 10. Ans (B) | 11. Ans.(B) | 12. Ans.(C) |
| 13. Ans.(C) | 14. Ans.(C) | 15. Ans.(C) |
| 16. Ans.(A) | 17. Ans.(B) | 18. Ans (D) |
| 19. Ans (C) | 20. Ans (D) | 21. Ans.(C) |
| 22. Ans.(C) | 23. Ans.(C) | 24. Ans.(B) |
| 25. Ans.(A) | 26. Ans.(B) | 27. Ans.(A) |
| 28. Ans.(A) | 29. Ans.(D) | 30. Ans.(D) |
| 31. Ans.(D) | 32. Ans.(B) | 33. Ans(C)  |
| 34. Ans (C) | 35. Ans.(D) |             |

**EXERCISE # O-II**

- |                                                                                                      |                  |                |
|------------------------------------------------------------------------------------------------------|------------------|----------------|
| 1. Ans. (C)                                                                                          | 2. Ans.(B)       | 3. Ans.(D)     |
| 4. Ans.(A,C)                                                                                         | 5. Ans.(B,C)     | 6. Ans.(A,C)   |
| 7. Ans.(A,B,D)                                                                                       | 8. Ans.(A,B,C,D) | 9. Ans.(A,B,D) |
| 10. Ans.(A,B,C,D)                                                                                    | 11. Ans.(B)      | 12. Ans.(D)    |
| 13. Ans.(C)                                                                                          | 14. Ans.(A)      | 15. Ans.(A)    |
| 16. Ans.(B)                                                                                          | 17. Ans.(D)      | 18. Ans.(C)    |
| 19. Ans.(B)                                                                                          | 20. Ans.(D)      | 21. Ans.(A)    |
| 22. Ans.(C)                                                                                          | 23. Ans.(A)      | 24. Ans.(D)    |
| 25. Ans.(A) $\rightarrow$ P, Q ; (B) $\rightarrow$ P,S ; (C) $\rightarrow$ P,R ; (D) $\rightarrow$ P |                  |                |
| 26. Ans.(A) $\rightarrow$ R,S ; (B) $\rightarrow$ P,Q,R,S ; (C) $\rightarrow$ Q                      |                  |                |
| 27. Ans.(A)                                                                                          | 28. Ans.(B)      |                |

**EXERCISE # J-MAIN**

- |              |              |              |
|--------------|--------------|--------------|
| 1. Ans.(2)   | 2. Ans.(3)   | 3. Ans.(2)   |
| 4. Ans.(4)   | 5. Ans.(3)   | 6. Ans.(3)   |
| 7. Ans.(1)   | 8. Ans.(1)   | 9. Ans.(3)   |
| 10. Ans.(1)  | 11. Ans.(1)  | 12. Ans.(3)  |
| 13. Ans.(3)  | 14. Ans.(2)  | 15. Ans.(1)  |
| 16. Ans.(3)  | 17. Ans.(3)  | 18. Ans.(2)  |
| 19. Ans.(2)  | 20. Ans.(1)  | 21. Ans.(2)  |
| 22. Ans.(2)  | 23. Ans.(4)  | 24. Ans.(1)  |
| 25. Ans.(3)  | 26. Ans.(3)  | 27. Ans. (4) |
| 28. Ans. (2) | 29. Ans. (2) | 30. Ans. (4) |

EXERCISE # J-ADVANCED

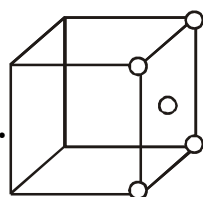
1. Ans.1.259

2. Ans.(A)

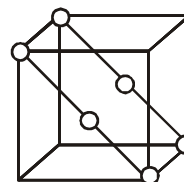
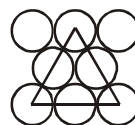
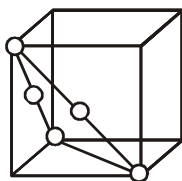
3. Ans. True

4. Ans.(D)

5. Ans.



fcc plan



6. Ans.(A)

7. Ans.18

8. Ans.(i) =  $5 \text{ kg m}^{-3}$

9. Ans.(B)

10. Ans. 117.1 pm

11. Ans. 216.5 pm

12. Ans. (A) P, S ; (B) -P,Q ; (C) - Q ; (D) - Q,R

13. Ans. (B)

14. Ans. (A)

15. Ans. (D)

16. Ans. (B,C)

17. Ans. (D)

18. Ans. (8)

19. Ans.(B)

20. Ans. (A)

21. Ans. (A)

22. Ans.(B,C,D)

23. Ans.(2)

24. Ans.(3)

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**IDEAL GAS**

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**1. INTRODUCTION**

Matter, as we know, broadly exist in three states - solid, liquid and gas.

There are always two opposite tendencies between particles of matter which determine the state of matter :

- Intermolecular forces.
- The molecular motion / random motion (energy of particles)

Intermolecular forces are the forces of attraction and repulsion between atoms or molecules. Attractive intermolecular forces are known as ***vander Waals forces***. These are dispersion forces, dipole-dipole forces & dipole induced forces. When two molecules are brought very close, they will exert repulsive forces. Magnitude of the repulsion rises very rapidly as the distance separating the molecules decreases.

This is the reason that liquid & solids are hard to compress. In these states, molecules are already in close contact, therefore they resist further compression (in that case repulsive interaction will increase)

Thermal energy is the energy of a body arising from motion of its atoms or molecules. It is directly proportional to the temperature of the substance. It is the measure of average kinetic energy of the particles of the matter and is thus responsible for movement of particles. This movement of particles is called ***thermal motion***. Intermolecular forces tend to keep the molecules together but thermal energy of the molecules tends to keep them apart. Three states of matter are the result of balance between intermolecular forces and the thermal energy of the molecules.

**2. GENERAL CHARACTERISTICS OF SOLID, LIQUID & GAS**

Each physical state of matter possesses characteristics properties of its own. For example,

**❖ Solids :**

All solids show the following characteristics :

- (i) Solids are rigid and incompressible.
- (ii) Solids have fixed shape and definite volume.
- (iii) Solids have their melting and boiling points above room temperature.
- (iv) Density of solid is high.

**❖ Liquids :**

All liquids show the following characteristics :

- (i) Liquids are almost incompressible but less incompressible than solids.
- (ii) Liquids have fixed volume but no fixed shape.
- (iii) Liquids have their melting points below room temperature and boiling points above room temperature, under normal conditions.
- (iv) Density of liquids is lower than that of solids but much higher than that of gases.

❖ **Gases :**

All gases show the following characteristics :

- (i) Gases are highly compressible, i.e. gases can be compressed easily by applying pressure.
- (ii) Gases have no fixed volume and shape. Gases fill the container of any size and shape completely.
- (iii) Gases can diffuse into each other rapidly.
- (iv) Gases have their melting and boiling points both below room temperature.
- (v) Gases generally have low density.

**3. MEASURABLE PROPERTIES OF GASES**

The characteristics of gases are described fully in terms of four parameters or measurable properties :

- (I) Amount of the gas (i.e., mass or number of moles).
- (II) Volume (V) of the gas.
- (III) Temperature (T)
- (IV) Pressure (P)

**I. Amount of the gas :**

- (i) The mass of a gas can be determined by weighing the container in which the gas is enclosed and again weighing the container after removing the gas. The difference between the two masses gives the mass of the gas.

$$\text{Mass of gas (m)} = \text{Mass of filled container} - \text{mass of empty container}$$

- (ii) The mass of the gas is related to the number of moles of the gas as

$$\text{Moles of gas (n)} = \text{Mass in grams} / \text{Molar mass} = m/M$$

- (iii) Mass is expressed in gram or kg.

**II. Gas volume :**

- (i) Since gases occupy the entire space available to them, the measurement of volume of a gas only requires a measurement of the container confining the gas.
- (ii) Volume is expressed in litres (L), millilitres (mL) or cubic centimeters (cm<sup>3</sup>) or cubic meters (m<sup>3</sup>).
- (iii) 1 L = 1000 mL ; 1 L = 1 dm<sup>3</sup> = 10<sup>-3</sup> m<sup>3</sup>  
 $1 \text{ m}^3 = 10^3 \text{ dm}^3 = 10^6 \text{ cm}^3 = 10^6 \text{ mL} = 10^3 \text{ L}$   
 1 mL or 1 cc = 1 cm<sup>3</sup>

**III. Temperature :**

- (i) Gases expand on increasing the temperature.
- (ii) Temperature is measured in degree centigrade (°C) or Celsius degree with the help of thermometers. Temperature is also measured in degree Fahrenheit (°F).
- (iii) S.I. unit of temperature is kelvin (K) or absolute degree  
 $K = ^\circ\text{C} + 273$
- (iv) Relation between °F and °C is  
 $^{\circ}\text{C}/5 = (^{\circ}\text{F} - 32) / 9$

Force exerted by the gas per unit area of the walls of the container in all directions. Thus,

❖ **Atmospheric pressure :**

The pressure exerted by atmosphere on earth's surface at sea level is called atmospheric pressure. Generally its unit is atm.

$$\begin{aligned} \text{Pressure}(P) &= \text{Force}(F) / \text{Area}(A) \\ &= \text{Mass}(m) \times \text{Acceleration}(g) / \text{Area}(a) \\ &= \text{Volume} \times \text{density} \times \text{Acceleration}(g) / \text{Area}(a) \\ &= \text{Area}(a) \times \text{height}(h) \times \text{density}(\rho) \times \text{Acceleration}(g) / \text{Area}(a) \end{aligned}$$

$$Pressure(P) = h\rho g$$

where  $h$  = Height of mercury column in the barometer.

$\rho$  = Density of mercury.

$g$  = Acceleration due to gravity.

Pressure does not depend on the cross section of tube, but only on the vertical height of the Hg. If area is doubled, volume also gets doubled and mass will also get doubled. Now it will rest on twice area but pressure exerted remains same.

$$1 \text{ atm} = 1.013 \text{ bar} = 1.013 \times 10^5 \text{ N/m}^2 = 1.013 \times 10^5 \text{ Pa}$$

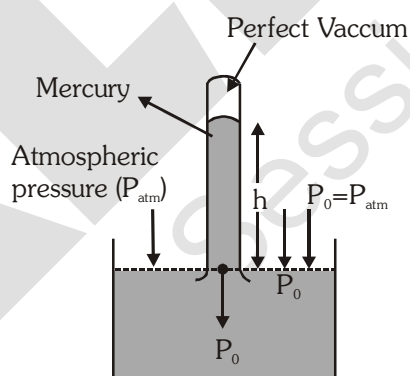
$$1 \text{ atm} = 76 \text{ cm of Hg} = 760 \text{ mm of Hg} = 760 \text{ torr}$$

## □ PRESSURE MEASURING DEVICES

Generally, the instruments used for the calculation of pressure of a gas are **barometer** and **manometer**.

(i) **Barometer** : A barometer is an instrument that is used for the measurement of atmospheric pressure.

The construction of the barometer is as follows -



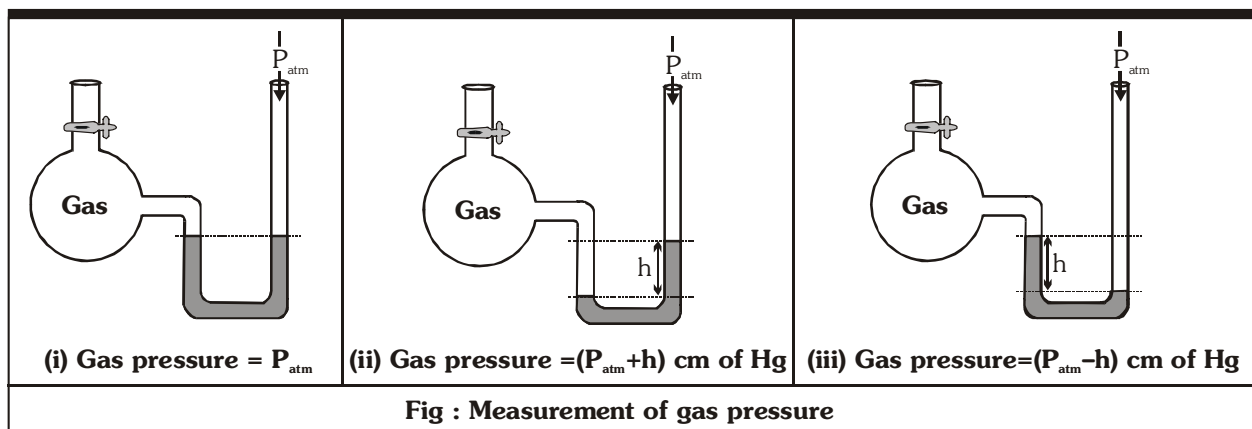
A thin narrow calibrated capillary tube is filled up to the brim, with a liquid such as mercury, and is inverted into a trough filled with the same fluid. Now depending on the external atmospheric pressure, the level of the mercury inside the tube will adjust itself, the reading of which can be monitored. When the mercury column inside the capillary comes to rest, then the net forces on the column should be balanced.

$$\Rightarrow P_0 \times A = \rho A \times gh$$

$$\Rightarrow \boxed{P_0 = \rho gh}$$
 ; where  $\rho$  is the density of the fluid.

(ii) **Manometer :**(a) **Open end manometer :**

It consists of a U-shaped tube partially filled with mercury. One limb of the tube is shorter than the other. The shorter limb is connected to the vessel containing the gas whereas the longer limb is open as shown in fig. The mercury in the longer tube is subjected to the atmospheric pressure while mercury in the shorter tube is subjected to the pressure of the gas.



Where  $P_{\text{atm}} = 76$  cm of Hg and  $h$  = Height in cm of Hg

There are three possibilities as described below :

- (i) If the level of Hg in the two limbs is same, then gas pressure = atmospheric pressure ( $P_{\text{atm}}$ ).
- (ii) If the level of Hg in the longer limbs is higher, gas pressure
 
$$= P_{\text{atm}} + (\text{difference between the two levels})$$

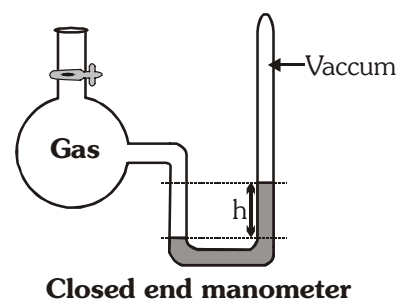
$$= P_{\text{atm}} + h.$$
- (iii) If the level of Hg in the shorter limb is higher, then gas pressure
 
$$= P_{\text{atm}} - (\text{difference between the two levels})$$

$$= P_{\text{atm}} - h.$$

(b) **Closed end manometer :**

This is generally used to measure low gas pressure.

It also consists of U-tube with one limb shorter than the other and partially filled with mercury as shown in fig. The space above mercury on the closed end is completely evacuated. The shorter limb is connected to the vessel containing gas. The gas exerts pressure on the mercury in the shorter limb and forces its level down.



**Gas pressure = [Difference in the Hg level in two limbs]**

**Ex.1 Why mercury is used in the barometer tube?**

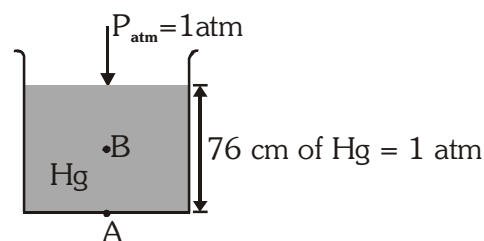
**Sol.** Mercury, a liquid with very high density, is normally used in the barometer because it does not stick to the surface of the glass tube. Mercury is also non-volatile at room temperature. Therefore, there are hardly any vapours of mercury above the liquid column and their pressure, if any, can be neglected. Due to high density of mercury, height of mercury column will be small and can be easily measured.

**Ex.2** An open tank is filled with Hg upto a height of 76cm.

Find the pressure at the

- Bottom (A) of the tank
- Middle (B) of the tank.

(If atmospheric pressure is 1 atm)



**Sol.** (a) At bottom,

$$P_A = P_{\text{atm}} + P_{\text{Hg}} \\ = 1 + 1 = 2 \text{ atm}$$

(b) At middle,

$$P_B = P_{\text{atm}} + P_{\text{Hg}} \\ = 1 + \frac{1}{2} = 1.5 \text{ atm}$$

**Ex.3** Find the height of water upto which water must be filled to create the same pressure at the bottom, as in above problem.

Given that  $d_w = 1 \text{ g/cm}^3$ ,  $d_{\text{Hg}} = 13.6 \text{ g/cm}^3$ ,  $h_{\text{Hg}} = 76 \text{ cm}$

**Sol.**  $P_{\text{water}} = P_{\text{Hg}}$

$$h_w d_w g = h_{\text{Hg}} d_{\text{Hg}} g$$

$$h_w d_w = h_{\text{Hg}} d_{\text{Hg}}$$

$$h_w \times 1 \text{ g/cm}^3 = 76 \text{ cm} \times 13.6 \text{ g/cm}^3$$

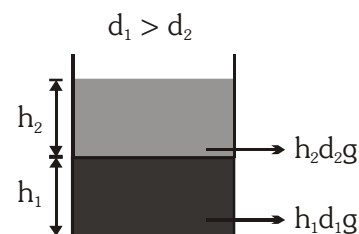
$$h_w = 1033.6 \text{ cm}$$

**Ex.4** What will be the pressure if two immiscible fluid is filled according to given diagram.

- Find the pressure at the bottom of tank.
- Find the pressure at the middle point of bottom layer.

**Sol.** (a)  $P_{\text{atm}} + h_2 d_2 g + h_1 d_1 g$  ;

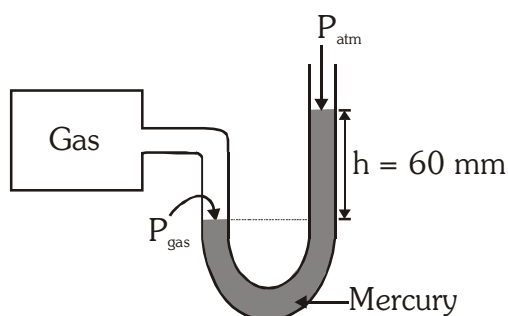
(b)  $P_{\text{atm}} + h_2 d_2 g + \frac{h_1}{2} d_1 g$





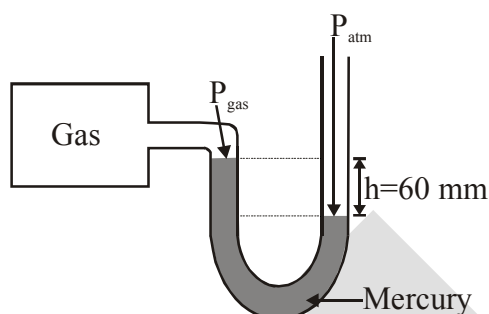
**Ex.5** Find the pressure of the gas inside a container if the open manometer attached to the container shows a difference of 60 mm.

**Sol. Case-I :**  $P_{\text{atm}} < P_{\text{gas}}$



$$\begin{aligned} P_{\text{gas}} &= P_{\text{atm}} + 60 \text{ mm} \\ &= 760 \text{ mm} + 60 \text{ mm} \\ &= 820 \text{ mm of Hg} \end{aligned}$$

**Case-II :**  $P_{\text{atm}} > P_{\text{gas}}$



$$\begin{aligned} P_{\text{atm}} &= P_{\text{gas}} + 60 \text{ mm} \\ 760 \text{ mm} &= P_{\text{gas}} + 60 \\ P_{\text{gas}} &= 700 \text{ mm} \end{aligned}$$

#### 4. GAS LAWS

The behaviour of the gases is governed by same general laws, which were discovered as a result of their experimental studies. These laws are relationships between measurable properties of gases. Some of these properties like pressure, volume, temperature and mass are very important because relationships between these variables describe state of the gas.

The first reliable measurement on properties of gases was made by Anglo-Irish scientist Robert Boyle in 1662. The law which he formulated is known as **Boyle's Law**. Later on attempts to fly in air with the help of hot air balloons motivated Jacques Charles and Joseph Lewis Gay Lussac to discover additional gas laws. Contribution from Avogadro and others provided lot of information about gaseous state.

##### 4.1 Boyle's Law :

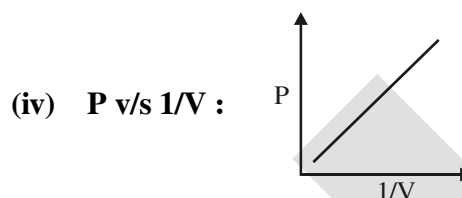
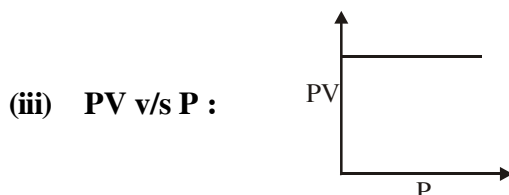
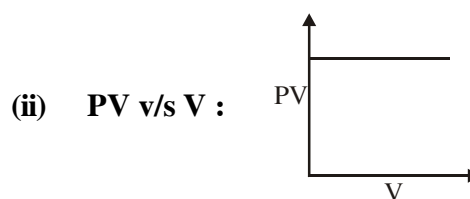
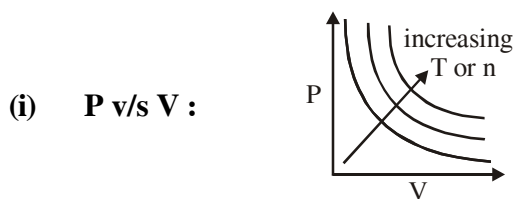
For a fixed amount of gas at constant temperature, the volume occupied by the gas is inversely proportional to the pressure applied on the gas or pressure of the gas.

$$\Rightarrow V \propto \frac{1}{P}$$

$$\Rightarrow \text{Hence, } PV = \text{const. (K)}$$

$$\Rightarrow \boxed{P_1 V_1 = P_2 V_2}$$

❖ **Graphical representation of Boyle's law :**



#### 4.2. Charle's Law :

For a fixed amount of gas at constant pressure, volume occupied by the gas is directly proportional to temperature of the gas on absolute scale of temperature.

$$\Rightarrow V \propto T$$

$$\Rightarrow V = KT$$

$$\frac{V}{T} = \text{constant (K)}$$

T = Temperature on absolute scale, kelvin scale or ideal gas scale.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\boxed{V = V_0 + bt}$$

$$\boxed{V = b'T}$$

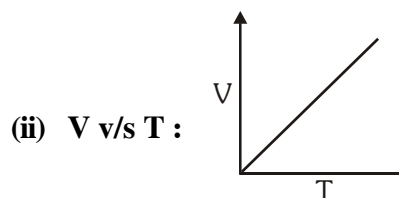
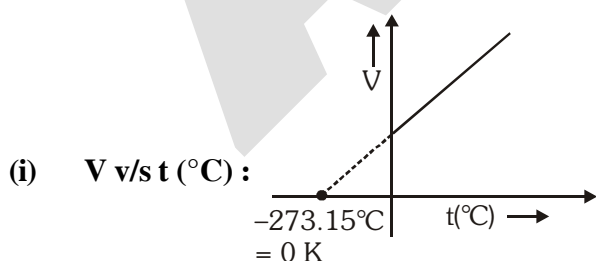
$t$  = temperature on centigrade scale.

$V_0$  = volume of gas at  $0^\circ\text{C}$ .

T = absolute temperature (K)

$$b, b' = \text{constants}$$

❖ **Graphical representation of Charle's Law :**



❖ **Important Points :**

- Since volume is proportional to absolute temperature, the volume of a gas should be theoretically zero at absolute zero temperature.
- In fact, no substance exists as gas at a temperature near absolute zero, though the straight line plots can be inter polated to zero volume. Absolute zero can never be attained practically though it can be approached only.
- By considering  $-273.15^{\circ}\text{C}$  as the lowest approachable limit, Kelvin developed temperature scale which is known as absolute scale.

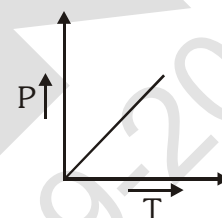
**4.3. Gay-lussac's law :**

For a fixed amount of gas at constant volume, pressure of the gas is directly proportional to temperature of the gas on absolute scale of temperature.

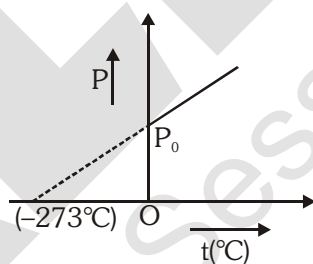
$$\Rightarrow P \propto T$$

$$\frac{P}{T} = \text{constant (K)}$$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \text{ Temperature on absolute scale, kelvin scale or ideal gas scale.}$$



**Note:** Originally, the law was developed on the centigrade scale, where it was found that pressure is a linear function of temperature  $\Rightarrow \boxed{P = P_0 + bt}$ , where 'b' is a constant and 'P<sub>0</sub>' is pressure at zero degree centigrade.



But for kelvin scale :  $\boxed{P = b''T}$  where T is in K.

**4.4. Avogadro's law :**

Equal volumes of all the gases under similar conditions of temperature and pressure contains equal number of molecules or moles of molecules (not atoms).

$$V \propto N \quad (\text{Temperature and pressure constant})$$

$$V \propto n \quad (\text{Temperature and pressure constant})$$

Where, N = number of molecules, n = number of moles of molecules

$$\boxed{\frac{V_1}{N_1} = \frac{V_2}{N_2} \text{ or } \frac{V_1}{n_1} = \frac{V_2}{n_2}}$$

Since volume of a gas is directly proportional to the number of moles; one mole of each gas at standard temperature and pressure (STP) will have same volume.

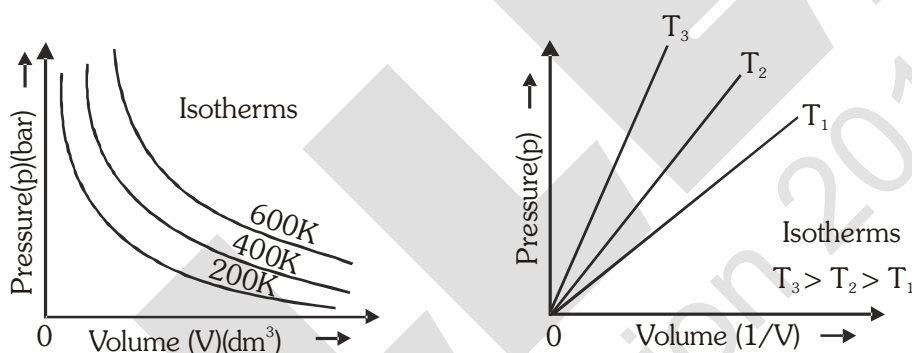
Standard temperature and pressure means 273.15 K (0°C) temperature and 1 bar (i.e., exactly  $10^5$  pascal) pressure. At STP, molar volume of an ideal gas or a combination of ideal gases is  $22.71098 \text{ L mol}^{-1}$ .

**Molar volume in litres per mole of some gases at 273.15 K and 1 bar (STP).**

|                |       |
|----------------|-------|
| Argon          | 22.37 |
| Carbon dioxide | 22.54 |
| Dinitrogen     | 22.69 |
| Dioxygen       | 22.69 |
| Dihydrogen     | 22.72 |
| Ideal gas      | 22.71 |

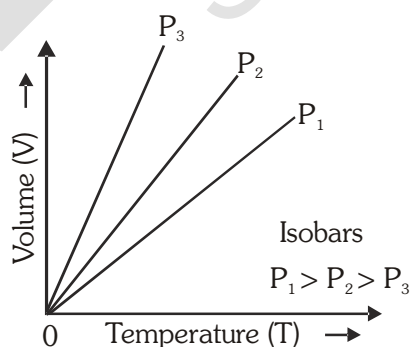
**Ex.6** What is a pressure-volume isotherm ?

**Sol.** Graph between P & V at constant temperature is called **PV-isotherm**.



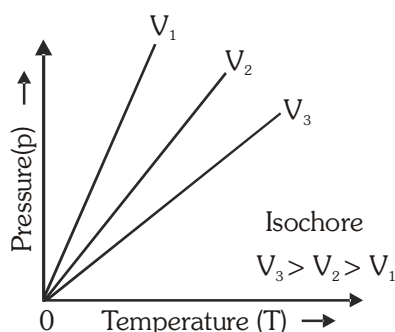
### Ex.7 What is Isobar ?

**Sol.** Graph plotted at constant pressure is called isobar. Graph between V & T at constant pressure is called VT-isobar.



**Ex.8** What is Isochore ?

**Sol.** Graph plotted at constant volume is called isochore. Graph between P & T at constant volume is called PT-isochore.



## 5. IDEAL GAS EQUATION

A single equation which is combination of Boyle's, Charle's & Avogadro's Law is known as **Ideal gas equation**. Or we can say a single equation which describe the simultaneous effects of the change in temperature & pressure on volume of the given amount of the gas is called the **Ideal gas equation**.

$$PV = nRT$$

According to Boyle's law,  $V \propto \frac{1}{P}$  (at constant T and n)

According to Charle's law,  $V \propto T$  (at constant P and n)

According to Avogadro's law,  $V \propto n$  (at constant T and P)

According to the three laws,  $V \propto \frac{nT}{P}$  or  $PV \propto nT$

or  $PV = nRT$  [Equation of state or combined gas law]

Where R is a constant called **Universal gas constant**, which does not depend on variables (P, V, n, T) and nature of gas.

- Molar volume is the volume of 1 mole of gas.

$$\text{Molar volume } (V_m) = \frac{\text{Volume}}{\text{mole}}$$

$$PV_m = RT$$

Volume of 1 mole of an ideal gas under STP conditions (273.15 K and 1 bar pressure) is  $22.7 \text{ L mol}^{-1}$ .

• **Dimension of R :**

$$R = \frac{PV}{nT} = \frac{\text{Pressure} \times \text{Volume}}{\text{Mole} \times \text{Temperature}} = \frac{(\text{Force} / \text{Area}) \times (\text{Area} \times \text{Length})}{\text{Mole} \times \text{Temperature (K)}}$$

$$= \frac{\text{Force} \times \text{Length}}{\text{Mole} \times \text{Temperature (K)}} = \frac{\text{Work or energy}}{\text{Mole} \times \text{Temperature (K)}}$$

• **Physical significance of R :**

The dimensions of R are energy per mole per kelvin and hence it represents the amount of work (or energy) that can be obtained from one mole of a gas when its temperature is raised by 1 K isobarically.

• **Units of R :**

(i) In lit-atm  $R = \frac{1 \text{ atm} \times 22.4 \text{ lit.}}{1 \text{ mol} \times 273 \text{ K}} = \mathbf{0.0821 \text{ lit-atm mol}^{-1} \text{K}^{-1}}$

(ii) In C.G.S system  $R = \frac{1 \times 76 \times 13.6 \times 980 \text{ dyne cm}^{-2} \times 22400 \text{ cm}^3}{1 \text{ mol} \times 273 \text{ K}}$   
 $= \mathbf{8.314 \times 10^7 \text{ erg mole}^{-1} \text{K}^{-1}}.$

(iii) In M.K.S.system  $R = \mathbf{8.314 \text{ Joule mole}^{-1} \text{K}^{-1}}.$   $[10^7 \text{ erg} = 1 \text{ joule}]$   
 (SI units)

(iv) In calories,  $R = \frac{8.314 \times 10^7 \text{ erg mole}^{-1} \text{K}^{-1}}{4.184 \times 10^7 \text{ erg}}$   
 $= 1.987 \approx \mathbf{2 \text{ calorie mol}^{-1} \text{K}^{-1}}.$

**Ex.9** A sample of gas occupies  $100 \text{ dm}^3$  at 1 bar pressure and at  $T^\circ \text{C}$ . If the volume of the gas is reduced to  $5 \text{ dm}^3$  at the same temperature, what additional pressure must be applied ?

**Sol.** From the given data :

$$P_1 = 1 \text{ bar} \quad P_2 = ?$$

$$V_1 = 100 \text{ dm}^3 \quad V_2 = 5 \text{ dm}^3$$

Since the temperature is constant, Boyle's law can be applied

$$P_1 V_1 = P_2 V_2 = P_2 = \frac{P_1 V_1}{V_2}$$

$$P_2 = \frac{(1 \text{ bar}) \times (100 \text{ dm}^3)}{(5 \text{ dm}^3)} = 20 \text{ bar}$$

$\therefore$  Additional pressure applied  $= 20 - 1 = \mathbf{19 \text{ bar}}$

**Ex.10** A human adult breathes in approximately  $0.50 \text{ dm}^3$  of air at 1.00 bar with each breath. If an air tank holds  $100 \text{ dm}^3$  of air at 200 bar, how many breathes the tank will supply ?

**Sol.** From the given data :

Volume of air in the tank ( $V_1$ )  $= 100 \text{ dm}^3$

Pressure of air in the tank ( $P_1$ ) = 200 bar

Pressure of air in each breath ( $P_2$ ) = 1 bar

$\therefore$  Volume of air at 1 bar pressure ( $V_2$ ) = ?

Since temperature is constant, Boyle's law is applicable

$$P_1 V_1 = P_2 V_2$$

or  $V_2 = \frac{P_1 V_1}{P_2}$

$$V_2 = \frac{(200 \text{ bar}) \times (100 \text{ dm}^3)}{(1 \text{ bar})} = 20,000 \text{ dm}^3$$

Volume of air breathed in each breath =  $0.50 \text{ dm}^3$

$$\text{Total no. of breathes the tank will supply} = \frac{\text{total volume of air}}{\text{volume of air in each breath}} = \frac{20000}{0.50}$$

**= 40,000 breaths.**

**Ex.11** A certain amount of a gas at  $27^\circ\text{C}$  and 1 bar pressure occupies a volume of  $25 \text{ m}^3$ . If the pressure is kept constant and the temperature is raised to  $77^\circ\text{C}$ , what will be the volume of the gas ?

**Sol.** From the available data :

$$V_1 = 25 \text{ m}^3 \quad T_1 = 27 + 273 = 300 \text{ K}$$

$$V_2 = ? \quad T_2 = 77 + 273 = 350 \text{ K}$$

Since the pressure of the gas is constant, Charles law is applicable

$$\frac{V_1}{V_2} = \frac{T_1}{T_2}$$

or  $V_2 = \frac{V_1 \times T_2}{T_1}$

$$V_2 = \frac{(25 \text{ m}^3) \times (350 \text{ K})}{(300 \text{ K})} = 29.17 \text{ m}^3$$

**Ex.12** A gas at a pressure of 5.0 bar is heated from  $0^\circ\text{C}$  to  $546^\circ\text{C}$  and simultaneously compressed to one third of its original volume. What will be the final pressure ?

**Sol.** From the available data :

$$V_1 = V \text{ dm}^3 \quad V_2 = \frac{V}{3} \text{ dm}^3$$

$$P_1 = 5 \text{ bar} \quad P_2 = ?$$

$$T_1 = 0 + 273 = 273 \text{ K} \quad T_2 = 546 + 273 = 819 \text{ K}$$

According to Gas equation  $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$  or  $P_2 = \frac{P_1 V_1 T_2}{T_1 V_2}$

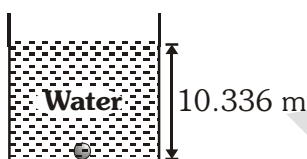
By substituting the values,  $P_2 = \frac{(5 \text{ bar}) \times (V \text{ dm}^3) \times (819 \text{ K})}{(273 \text{ K}) \times (V/3 \text{ dm}^3)} = 45 \text{ bar}$

**Ex.13** The density of a gas is found to be  $1.56 \text{ g dm}^{-3}$  at  $0.98 \text{ bar}$  pressure and  $65^\circ\text{C}$ . Calculate the molar mass of the gas. Use  $R = 0.083 \text{ dm}^3 \text{ bar K}^{-1} \text{ mol}^{-1}$

**Sol.** We know that :

$$M = \frac{dRT}{P} = \frac{(1.56 \text{ g dm}^{-3}) \times (0.083 \text{ dm}^3 \text{ bar K}^{-1} \text{ mol}^{-1}) \times 338 \text{ K}}{(0.98 \text{ bar})} = 44.66 \text{ g mol}^{-1}$$

**Ex.14** (a) Radius of a bubble at the bottom of the tank shown below was found to be  $1 \text{ cm}$ , then find the radius of the bubble at the surface of water considering the temperature at the surface & bottom being same.



(b) If absolute temperature at the surface is 4 times that at the bottom, then find radius of bubble at the surface.

**Sol.**

(a)  $\frac{P_b V_b}{n_b T_b} = \frac{P_s V_s}{n_s T_s}$

$$2 \times \frac{4}{3} \pi r_b^3 = 1 \times \frac{4}{3} \pi r_s^3$$

$$2 \times 1^3 = r_s^3$$

$$r_s = 2^{1/3} \text{ cm}$$

(b) Given that  $T_s = 4 \times T_b$

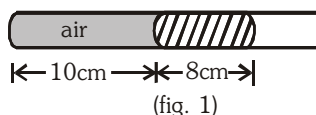
$$\frac{P_b V_b}{n_b T_b} = \frac{P_s V_s}{n_s T_s}$$

$$2 \times \frac{\frac{4}{3} \pi r_b^3}{T_b} = 1 \times \frac{\frac{4}{3} \pi r_s^3}{4 \times T_b}$$

$$r_s^3 = 8$$

$$r_s = 2 \text{ cm}$$

**Ex.15** A  $10 \text{ cm}$  length of air is trapped by a column of Hg,  $8 \text{ cm}$  long in capillary tube horizontally fixed as shown below at  $1 \text{ atm}$  pressure.



Calculate the length of air column when the tube is fixed at same temperature.

- Vertically with open end up
- Vertically with open end down
- At an angle of  $45^\circ$  from horizontal with open end up





- Sol.** (a) When the capillary tube is held vertically with open end up (fig.2),  
The pressure on the air column = atmospheric pressure + pressure  
of 8 cm Hg column

$$= 76 + 8 = 84 \text{ cm of Hg.}$$

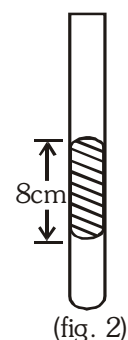
Let, at this condition the length of the air column =  $\ell_2$

and the length of air column when capillary is horizontally fixed

$$= \ell_1 = 10 \text{ cm and pressure on air column} = 1 \text{ atm.}$$

Let the cross section area of the capillary =  $a \text{ cm}^2$

$$\therefore 76 \times 10 \times a = 84 \times \ell_2 \times a \quad \text{or} \quad \ell_2 = \frac{76 \times 10}{84} = \mathbf{9.04 \text{ cm}}$$



- (b) When the capillary tube is held vertically with open end down (fig.3), the pressure on the air column

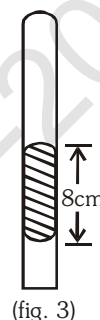
= atmospheric pressure – pressure of 8 cm Hg column

$$= 76 - 8 = 68 \text{ cm of Hg.}$$

Let at this condition the length of air column =  $\ell_3$ .

$$\therefore 68 \times \ell_3 \times a = 76 \times 10 \times a$$

$$\text{or } \ell_3 = \frac{76 \times 10}{68} = \mathbf{11.17 \text{ cm}}$$



- (c) When the capillary is held at  $45^\circ$  with open end up, the weight of Hg is partially borne by the gas and partially by the Hg. The pressure on the gas due to Hg column

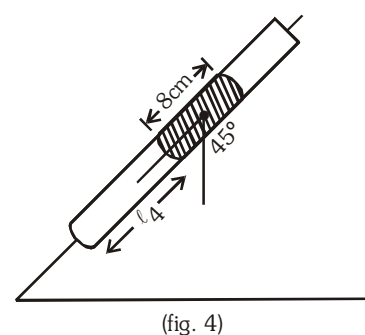
$$= 8 \times \sin 45^\circ = 8 \times \frac{1}{\sqrt{2}} = \frac{8}{\sqrt{2}} \text{ cm of Hg}$$

$$\therefore \text{total pressure on the gas} = \left( 76 + \frac{8}{\sqrt{2}} \right) \text{ cm of Hg.}$$

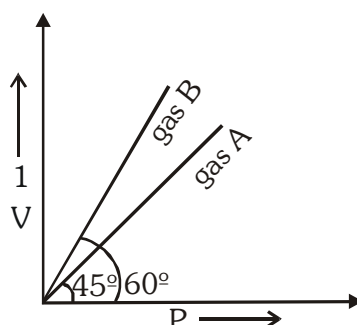
Let length of air column at this pressure =  $\ell_4$ .

$$\therefore \ell_4 \times a \times \left( 76 + \frac{8}{\sqrt{2}} \right) = 10 \times a \times 76$$

$$\therefore \ell_4 = \left( \frac{10 \times 76}{76 + 8/\sqrt{2}} \right) = \mathbf{9.3 \text{ cm}}$$



**Ex.16** At constant temperature of 273 K,  $\left(\frac{1}{V}\right)$  v/s  $P$  are plotted for two ideal gases A and B as shown.



Find out the number of moles of gas A and B.

**Sol.**  $PV = nRT$ ,  $P = \frac{1}{V} nRT \Rightarrow \frac{1}{V} = \frac{1}{nRT} P$

Comparing by equation :  $y = mx + C$

$C = 0$

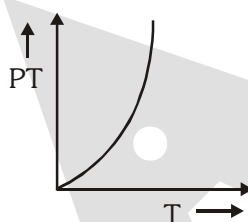
$m = \frac{1}{nRT} \quad (\because m = \tan \theta)$

$\tan \theta = \frac{1}{nRT}$

$n_A = \frac{1}{RT \tan \theta} \Rightarrow n_A = \frac{1}{0.0821 \times 273 \times \tan 45^\circ} \Rightarrow n_A = \frac{1}{22.4}$

$n_B = \frac{1}{RT \tan 60^\circ} = \frac{1}{22.4 \sqrt{3}}$

- Ex.17** (a) Plot the curve between  $PT$  vs  $T$  at const  $V$  & constant no. of moles.  
 (b) Find the number of moles of gas taken when the volume of the vessel is 82.1 ml and  $\frac{d}{dT} [PT]$  at 300 K = 300 for the given curve.



**Sol.**

(a)

(b) From graph,  $P = KT \Rightarrow PT = KT^2$

$\frac{d(PT)}{dT} = 2KT$

$300 = 2 K \times 300$

$K = \frac{1}{2}$

$\frac{nR}{V} = \frac{1}{2} \Rightarrow \frac{n \times 0.0821}{0.0821} = \frac{1}{2} \Rightarrow n = \frac{1}{2}$

**Ex.18** A glass bulb of 2 L capacity is filled by helium gas at 10 atm pressure. Due to a leakage the gas leaks out. What is the volume of gas leaked if the final pressure in container is 1 atm.

**Sol.**  $P_1 \times 2 \text{ L} = P_2 \times V$

$$\Rightarrow 10 \times 2 = 1 \times V$$

$$\Rightarrow 20 = V$$

$$V = V' + 2 \text{ L}$$

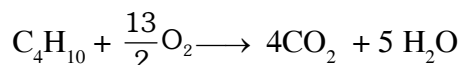
$$20 = V' + 2 \text{ L}$$

$$V' = 18 \text{ L}$$

$\Rightarrow$  total volume of gas leaked

**Ex.19** LPG is a mixture of n-butane & iso-butane. What is the volume of oxygen needed to burn 1 kg of LPG at 1 atm, 273 K ?

**Sol.** During the burning of LPG following reaction takes place -



Now, for complete combustion of 1 mole of LPG  $\longrightarrow \frac{13}{2}$  moles of  $\text{O}_2$  are required.

$\therefore$  for  $\frac{1000}{58}$  moles of LPG  $\longrightarrow \frac{13}{2} \times \frac{1000}{58}$  moles of  $\text{O}_2$  are required.

Thus, the volume of oxygen needed to burn 1 kg of LPG at 1 atm & 273K would be

$$\text{Vol. of } \text{O}_2 = \text{Moles of } \text{O}_2 \times 22.4 \text{ L} = \frac{13}{2} \times \frac{1000}{58} \times 22.4 = \mathbf{2510 \text{ L}}$$

**Ex.20** 3.6 g of an ideal gas was injected into a bulb of internal volume of 8 L at pressure P atm and temp T K. The bulb was then placed in a thermostat maintained at  $(T + 15)\text{K}$ , 0.6 g of the gas was let off to keep the original pressure. Find P and T if mol weight of gas is 44.

**Sol.** Here, we are given with 2 conditions.

Initially :

Pressure,  $P_1 = P \text{ atm}$

Volume,  $V_1 = 8 \text{ L}$

$$\text{Moles, } n_1 = \frac{3.6}{44}$$

Temperature  $T_1 = T \text{ K}$

Finally  $\Rightarrow$  At  $(T + 15)\text{K}$  0.6 g of gas was let off to keep pressure constant.

$\therefore$  Pressure,  $P_2 = P \text{ atm}$

Volume,  $V_2 = 8 \text{ L (const.)}$

$$\text{Moles, } n_2 = \frac{3}{44}$$

Temp,  $T_2 = (T + 15) \text{ K}$

Now, applying -

$$\frac{P_1 V_1}{n_1 T_1} = \frac{P_2 V_2}{n_2 T_2}$$

$$\Rightarrow \frac{P \times 8}{\frac{3.6}{44} \times T} = \frac{P \times 8}{\left(\frac{3}{44}\right) \times (T + 15)}$$

$$T = 75 \text{ K}$$

Now, putting the value of temp. in the following equation we get :

$PV = nRT$  (putting initial condition)

$$P(8) = \frac{3.6}{44}(0.08)(75)$$

$$\Rightarrow P = 0.062 \text{ atm}$$

**Ex.21** The best vacuum so far attained in laboratory is  $10^{-10}$  mm of Hg. What is the number of molecules of gas remain per  $\text{cm}^3$  at  $20^\circ\text{C}$  in this vacuum ?

**Sol.** Given conditions -

$$P = 10^{-10} \text{ mmHg} = \frac{10^{-10}}{760} \text{ atm} ; V = 1 \text{ cm}^3 = \frac{1}{1000} \text{ L} ; T = 20^\circ\text{C} = 293 \text{ K}$$

No. of molecules,  $N = ?$

Now, applying

$$PV = nRT$$

$$\therefore \text{number of molecules per cm}^3, N = \frac{N_A \times P \times V}{RT}$$

$$\Rightarrow N = \frac{6.023 \times 10^{23} \times (10^{-10}/760) \times (1/1000)}{(0.0821)(293)}$$

$$N = 3.29 \times 10^6 \text{ molecules}$$

## 6. DALTON'S LAW OF PARTIAL PRESSURES

### 6.1 Partial pressure :

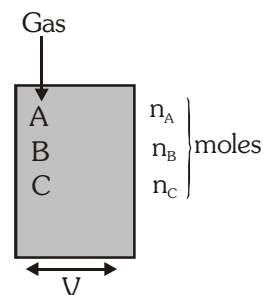
In a mixture of non-reacting gases, partial pressure of any component gas is defined as the pressure exerted by the individual gas if whole of the volume of mixture had been occupied by this component only.

Partial pressure of component gases are -

$$P_A = \frac{n_A RT}{V} = \text{partial pressure of A}$$

$$P_B = \frac{n_B RT}{V} = \text{partial pressure of B}$$

$$P_C = \frac{n_C RT}{V} = \text{partial pressure of C}$$



## 6.2 Dalton's Law :

Dalton's law of partial pressure states "at a given temperature, the total pressure exerted by two or more non-reacting gases occupying a definite volume is equal to the sum of the partial pressures of the component gases."

$$P_{\text{Total}} = p_1 + p_2 + p_3 + \dots \quad (\text{At constant } V \text{ and } T)$$

$$= \left( \frac{n_1}{V} + \frac{n_2}{V} + \frac{n_3}{V} + \dots \right) RT = (n_1 + n_2 + n_3 + \dots) \frac{RT}{V} = \frac{nRT}{V}$$

Where  $n = n_1 + n_2 + n_3 + \dots = \text{Total moles}$ ,  $V = \text{Total volume}$

$$P_{\text{Total}} = \sum p_i = \frac{RT}{V} \sum n_i$$

- Dalton's law of partial pressure is applicable only to non-reacting gases.

If the two non-reacting gases A and B having  $n_A$  and  $n_B$  number of moles respectively are filled in a vessel of volume  $V$  at temperature  $T$ , then

$$\frac{p_A}{P} = \frac{n_A RT / V}{(n_A + n_B) RT / V} = \frac{n_A}{n_A + n_B} = x_A \quad (\text{mole fraction of A})$$

$$p_A = x_A \times P, \quad \text{Similarly } p_B = x_B \times P$$

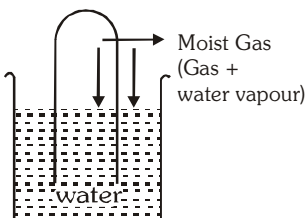
**Partial pressure of a component = Mole fraction  $\times$  total pressure.**

- 6.3 It has been observed that gases are generally collected over water and therefore are moist.

$$P_{\text{dry gas}} = P_{\text{moist gas}} - P_{\text{water vapour}}$$

**or Pressure of dry gas = Pressure of moist gas – aqueous tension**

The pressure exerted by water vapour is constant when it is in equilibrium with liquid water at a particular temperature. It is called vapour pressure of water or **aqueous tension**, which varies with the temperature and becomes 760 mm at 100°C.



6.4 Relative Humidity (RH) =  $\frac{\text{Partial pressure of water in air}}{\text{Vapour pressure of water (aq. tension)}}$

## 7. AMAGAT'S LAW OF PARTIAL VOLUME

### 7.1 Partial Volume :

Partial volume of any component is defined as the volume occupied by that particular component when it is kept at same total pressure and temperature as of the mixture.

### 7.2 Amagat's law :

According to this law at constant temperature and pressure, the total volume of mixture of non-reacting gases is equal to the sum of partial volumes of each component present in mixture.

$$V_T = V_1 + V_2 + V_3 + \dots$$

Let us consider three non-reacting gases A, B and C are present in a container which have no. of moles  $n_A$ ,  $n_B$  and  $n_C$  respectively. For each gas partial volume is

$$V_A = n_A \left( \frac{RT}{P} \right) = \text{partial volume of A}$$

$$V_B = n_B \left( \frac{RT}{P} \right) = \text{partial volume of B}$$

$$V_c = n_c \left( \frac{RT}{P} \right) = \text{partial volume of C}$$

- **Total volume :**

$$V_T = V_A + V_B + V_C = (n_A + n_B + n_C) \left( \frac{RT}{P} \right) = n_T \left( \frac{RT}{P} \right)$$

$$\frac{V_A}{V_T} = \frac{n_A}{n_T} = x_A \quad (\text{Mole fraction of gas A})$$

$$\frac{V_B}{V_T} = \frac{n_B}{n_T} = x_B \quad (\text{Mole fraction of gas B})$$

$$\frac{V_C}{V_T} = \frac{n_C}{n_T} = x_C \quad (\text{Mole fraction of gas C})$$

$$\therefore \text{Partial volume of a gas} = \text{Mole fraction} \times \text{Total volume}$$

**Ex.22** (a) Find the total pressure and partial pressure of each component if a container of volume 8.21 lit. contains 2 moles of A and 3 mole of B at 300K.

(b) What will be the final pressure and partial pressure of each component if 5 moles of C is also added to the container at same temperature.

**Sol.**

$$(a) \quad P_A = \frac{n_A RT}{V} = \frac{2 \times 0.821 \times 300}{8.21} = 6 \text{ atm}$$

$$P_B = \frac{n_B RT}{V} = \frac{3 \times 0.821 \times 300}{8.21} = 9 \text{ atm}$$

Total pressure  $P_T = P_A + P_B = 6 + 9 = 15 \text{ atm}$

$$(b) \quad P_c = \frac{n_c RT}{V} = \frac{5 \times 0.821 \times 300}{8.21} = 15 \text{ atm}$$

**Note:** If we add or remove a non reacting gas partial pressure of other gases remains unchanged.

$$P_T = P_A + P_B + P_C = 6 + 9 + 15 = 30 \text{ atm}$$

**Ex.23** If 2 lit. of gas A at 1.5 atm and 3 lit. of gas B at 2 atm are mixed in a 5 lit. container then find the final pressure, considering all are at same temperature.

**Sol.**  $n_A = \frac{P_A V_A}{RT} = \frac{2 \times 1.5}{RT} = \frac{3}{RT}$

$$n_B = \frac{P_B V_B}{RT} = \frac{3 \times 2}{RT} = \frac{6}{RT}$$

$$\therefore n_T = n_A + n_B$$

$$\frac{P_T V_T}{RT} = \frac{3}{RT} + \frac{6}{RT}$$

$$P_T \times 5 = 3 + 6$$

$$P_T = 1.8 \text{ atm}$$

**Ex.24** One mole of  $N_2$  and 3 moles of  $H_2$  are taken in a container of capacity 8.21 lit. at 300 K to produce  $NH_3$ . Find the partial pressures of  $N_2$  and  $H_2$  if partial pressure of  $NH_3$  after sufficient time was found to be 3 atm.



mole at  $t = 0$       1      3

mole at  $t = t_{eq}$        $1-x$        $3-3x$        $2x$

Given that

$$P_{NH_3} = 3$$

$$\frac{n_{NH_3} RT}{V} = 3$$

$$\frac{2x \times 0.0821 \times 300}{8.21} = 3$$

$$x = \frac{1}{2}$$

$$n_{N_2} = 1 - x = \frac{1}{2}$$

$$n_{H_2} = 3 - 3x = \frac{3}{2}$$

$$n_{NH_3} = 2x = 1$$

$$P_{N_2} = \frac{n_{N_2} RT}{V} = \frac{1}{2} \times \frac{0.0821 \times 300}{8.21} = 1.5 \text{ atm}$$

$$P_{H_2} = \frac{n_{H_2} RT}{V} = \frac{3}{2} \times \frac{0.0821 \times 300}{8.21} = 4.5 \text{ atm}$$

**Ex.25** 2 moles of  $\text{NH}_3(\text{g})$  and 1 mole of  $\text{HCl}(\text{g})$  are taken in a container of capacity 8.21 lit at 300K to produce  $\text{NH}_4\text{Cl}(\text{s})$ . Find the total pressure after the reaction.

**Sol.**  $\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \longrightarrow \text{NH}_4\text{Cl}(\text{s})$

initial        2            1

after rxn     1            0

In this reaction  $\text{HCl}$  is L.R. so it will be completely consumed. We don't consider pressure due to solid.

$$\therefore P_T = \frac{nRT}{V} = \frac{1 \times 0.821 \times 300}{8.21} = 3 \text{ atm}$$

**Ex.26** A closed container containing  $\text{O}_2$  and some liquid water was found to exert 740 mm pressure at  $27^\circ\text{C}$ .

- Then calculate the pressure exerted by  $\text{O}_2$  if aqueous tension at  $27^\circ\text{C}$  is 20 mm.
- What will be the final pressure if volume is reduced to half.  
(consider volume of liquid water negligible)
- What will be the final pressure if volume is doubled.

**Sol.** (a)  $P_T = P_{\text{dry gas}} + P_{\text{aq. tension}}$

$$740 = P_{\text{O}_2} + 20$$

$$P_{\text{O}_2} = 740 - 20 = 720 \text{ mm}$$

(b)  $(P_{\text{O}_2} V_{\text{O}_2})_{\text{initial}} = (P_{\text{O}_2} V_{\text{O}_2})_{\text{final}}$  (Boyle's law)

$$720 \times V = P_{\text{O}_2} \times \frac{V}{2}$$

$$P_{\text{O}_2} = 1440 \text{ mm}$$

$$P_T = P_T = P_{\text{O}_2} + P_{\text{aq.}}$$

$$= 1440 + 20 = 1460 \text{ mm}$$

(c)  $(P_{\text{O}_2} V_{\text{O}_2})_{\text{initial}} = (P_{\text{O}_2} V_{\text{O}_2})_{\text{final}}$

$$720 \times V = P_{\text{O}_2} \times 2V$$

$$P_{\text{O}_2} = 360 \text{ mm}$$

$$P_T = P_{\text{O}_2} + P_{\text{aq.}}$$

$$= 360 + 20 = 380 \text{ mm}$$





**Ex.29** What is the difference in the density of dry air at 1 atm and 25°C and moist air with 50% relative humidity under the same condition. The vapour pressure of water at 25°C is 23.7 Torr and dry air has 75.5% N<sub>2</sub> and 24.5% O<sub>2</sub>.

**Sol.**  $M(\text{dry air}) = \frac{M_1(\text{O}_2)X_1(\% \text{ of O}_2) + M_2(\text{N}_2)X_2(\% \text{ of N}_2)}{X_1 + X_2}$

$$= \frac{32 \times 24.5 + 28 \times 75.5}{100} = 28.98 \text{ g mol}^{-1}$$

$$d(\text{dry air}) = \frac{PM(\text{air})}{RT} = \frac{1 \times 28.98}{0.0821 \times 298} = 1.184 \text{ g L}^{-1}$$

$$= 1.184 \text{ kg m}^{-3} \left( \because 1 \text{ g L}^{-1} = \frac{10^{-3} \text{ kg}}{10^{-3} \text{ m}^3} = 1 \text{ kg m}^{-3} \right)$$

$$\text{Relative humidity (50\%)} = \frac{\text{partial pressure of H}_2\text{O in air}}{\text{vapour pressure of H}_2\text{O}}$$

$$\therefore P(\text{H}_2\text{O}) = 0.50 \times 23.7 \text{ Torr} = 11.85 \text{ torr} = \frac{11.85}{760} \text{ atm} = 0.0156 \text{ atm}$$

$$\% \text{ of H}_2\text{O vapour in air} = \frac{0.0156 \times 100}{1} = 1.56\%$$

$$\% \text{ of N}_2 \text{ and O}_2 \text{ in air} = 98.44\%$$

$$M(\text{wet air}) = \frac{28.98 \times 98.44(\text{air}) + 18 \times 1.56(\text{water vapour})}{100} = 28.81 \text{ g mol}^{-1}$$

$$d(\text{wet air}) = \frac{PM(\text{wet air})}{RT} = \frac{1 \times 28.81}{0.0821 \times 298}$$

$$= 1.177 \text{ g L}^{-1} = 1.177 \text{ kg m}^{-3}$$

$$\text{difference} = 1.184 - 1.177 = 0.007 \text{ kg m}^{-3}$$

**Ex.30** A gaseous mixture at 760 mm in a cylinder has 65% N<sub>2</sub>, 15% O<sub>2</sub> and 20 % CO<sub>2</sub> by volume. Calculate the partial pressure of each gas.

**Sol.** Partial pressure of gas = mole fraction of gas × total pressure = volume fraction of gas × total pressure

$$p_{\text{N}_2} = \frac{65}{100} \times 760 = 494 \text{ mm}$$

$$p_{\text{O}_2} = \frac{15}{100} \times 760 = 114 \text{ mm}$$

$$p_{\text{CO}_2} = \frac{20}{100} \times 760 = 152 \text{ mm}$$

## 8. PROBLEM RELATED WITH DIFFERENT TYPE OF CONTAINERS

## I. Closed Container :

In this case gas can neither go outside nor it can come inside. So number of moles of gas is always constant.

Closed container can be of following types -

(a) **Closed rigid container** : In this case number of moles constant, volume constant.

At this condition :

Initial                      Final

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

Example : Gas cylinder

(b) **Closed non rigid container : (fitted with freely movable piston)**

In this kind of container inside pressure is always equal to outside pressure, i.e., atmospheric pressure so that  $n = \text{constant}$ ,  $p = \text{constant}$

**Ex:** Balloon, Water bubble

Initial                      Final

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

**Ex.31** A balloon is inflated to  $\frac{7}{8}$  of its maximum volume at  $27^\circ\text{C}$  then calculate the minimum temperature above which it will burst.

**Sol.** 
$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\frac{7V}{8 \times 300} = \frac{V}{T}$$

$$T = 342.8 \text{ K}$$

**Ex.32** A gas cylinder containing cooking gas can with stand a pressure of 18 atm. The pressure gauge of cylinder indicates 12 atm at  $27^\circ\text{C}$ . Due to sudden fire in building the temperature start rising at what temperature will the cylinder explode.

**Sol.** 
$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$\frac{12}{300} = \frac{18}{T}$$

$$T = 450 \text{ K}$$



**Ex.34** An open flask contains air at 27°C. Calculate the temperature at which it should be heated so that

- (a)  $1/3^{\text{rd}}$  of air measured in the container at 27°C escape out.  
 (b)  $1/3^{\text{rd}}$  of air measured in the container at final temperature escape out.

**Sol.**

(a)  $n_{\text{initial}} - n_{\text{final}} = n_{\text{expelled}}$

$$\frac{PV}{R \times 300} - \frac{PV}{R \times T} = \frac{1}{3} \times \frac{PV}{R \times 300}$$

$$\frac{1}{300} - \frac{1}{T} = \frac{1}{900}$$

$$\frac{1}{T} = \frac{1}{300} - \frac{1}{900} = \frac{3-1}{900} = \frac{2}{900}$$

$$\Rightarrow T = 450 \text{ K} = 177^\circ\text{C}$$

(b)  $n_{\text{initial}} - n_{\text{final}} = n_{\text{expelled}}$

$$\frac{PV}{R \times 300} - \frac{PV}{R \times T} = \frac{1}{3} \times \frac{PV}{R \times T}$$

$$\frac{1}{300} - \frac{1}{T} = \frac{1}{3 \times T}$$

$$\Rightarrow T = 400 \text{ K} = 127^\circ\text{C}$$

**Ex.35** A bulb of unknown volume containing air is heated from 27°C to 227°C at constant pressure. The expelled air is measured at different temperature of determine volume of container. What will be volume of container if -

- (a) 200 ml of air measured at 227°C was expelled.  
 (b) 200 ml of air measured at 27°C was expelled.  
 (c) 200 ml of air measured at 127°C was expelled.

**Sol.**

(a)  $n_{\text{initial}} - n_{\text{final}} = n_{\text{expelled}}$

$$\frac{PV}{R \times 300} - \frac{PV}{R \times 500} = \frac{P \times 200}{R \times 500}$$

$$\frac{V}{3} - \frac{V}{5} = \frac{200}{5}$$

$$\frac{5V - 3V}{15} = \frac{200}{5}$$

$$\Rightarrow 2V = \frac{200 \times 15}{5} \Rightarrow V = 300 \text{ ml}$$

(b)  $\frac{PV}{R \times 300} - \frac{PV}{R \times 500} = \frac{P \times 200}{R \times 300}$

$$\frac{2V}{15} = \frac{200}{3} \Rightarrow V = \frac{100 \times 15}{2 \times 3} = 500 \text{ ml}$$

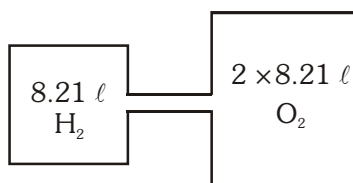
(c)  $\frac{PV}{R \times 300} - \frac{PV}{R \times 500} = \frac{P \times 200}{R \times 400}$

$$\frac{2V}{15} = \frac{200}{4} \Rightarrow V = \frac{200 \times 15}{2 \times 4} = 375 \text{ ml}$$

#### IV. Connected Container :

If containers are connected for substantial time then gases move from one container to another container till partial pressure of each component of mixtures becomes equal in all connected containers (irrespective whether containers have same or different temperature and volumes)

**Ex.36** A container of 8.21 lit. capacity is filled with 1 mole of  $H_2$  at 300 K and it is connected to another container of capacity  $2 \times 8.21$  lit. containing 4 moles of  $O_2$  at 300 K, then find the final pressure & partial pressure of each gas.



**Sol.**  $P_f V_f = n_f RT$   
 $P_f (3 \times 8.21) = 5 \times 0.0821 \times 300$   
 $P_f = 5 \text{ atm}$

$$P_{H_2} = x_{H_2} P_f = \frac{1}{1+4} \times 5 = 1 \text{ atm}$$

$$P_{O_2} = x_{O_2} P_f = \frac{4}{1+4} \times 5 = 4 \text{ atm}$$

**Ex.37** A 10 litre container consist of 1 mole of gas at 300 K. It is connected to another container having volume 40 litre and is initially at 300 K. The nozzle connecting two containers is opened for a long time and once the movement of gas stopped, the larger container was heated to a temperature of 600 K. Calculate

- Moles and pressure of gas in both the containers before heating.
  - Moles and pressure in two containers after heating.
- (Assume that initially the larger container is completely evacuated.)

**Sol.** (a) Before heating :

$$P_I = P_{II}$$

$$\frac{(1-x)R \times 300}{10} = \frac{x \times R \times 300}{40}$$

$$x = 0.8 \text{ moles}$$

$$n_I = 1 - x = 0.2 \text{ mole}$$

$$n_{II} = x = 0.8 \text{ mole}$$

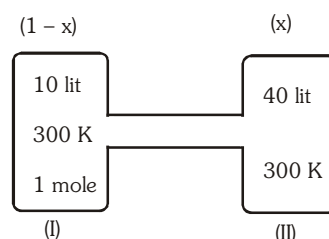
$$\text{Pressure} = \frac{x \times R \times T}{V} = \frac{0.8 \times R \times 300}{40} = 0.492 \text{ atm}$$

(b) After heating :

$$\frac{(1-x_1)R \times 300}{10} = \frac{x_1 \times R \times 600}{40}$$

$$x_1 = 0.67 \text{ moles, Given } T_1 = 600 \text{ K}$$

$$\text{Pressure} = \frac{x_1 \times R \times T_1}{V} = \frac{0.67 \times 0.0821 \times 600}{40} = 0.821 \text{ atm}$$



**Ex.38** One litre flask contains air, water vapour and a small amount of liquid water at a pressure of 200 mmHg. If this is connected to another one litre evacuated flask, what will be the final pressure of the gas mixture at equilibrium? Assume that temperature to be 50°C. Aqueous tension at 50°C = 93 mmHg.

### 9.3 Graham's Law :

Under similar condition of pressure (partial pressure) and temperature, the rate of diffusion of different gases is inversely proportional to square root of their density.

$$\Rightarrow \text{rate of diffusion, } r \propto \frac{1}{\sqrt{d}}$$

$$\Rightarrow \frac{r_1}{r_2} = \frac{\sqrt{d_2}}{\sqrt{d_1}} = \frac{\sqrt{M_2}}{\sqrt{M_1}} = \frac{\sqrt{V.D_2}}{\sqrt{V.D_1}}$$

where,  $d$  = density of gas

$V.D$  = vapour density

$M$  = molar mass of gas

- Under conditions of same temperature but different pressure, we have -

$$r \propto \frac{P}{\sqrt{M}}$$

$$\frac{r_1}{r_2} = \frac{P_1}{P_2} \sqrt{\frac{M_2}{M_1}}$$

If both gases are present in the same container at same temperature.

$$P \propto n$$

$$\Rightarrow \frac{r_1}{r_2} = \frac{n_1}{n_2} \sqrt{\frac{M_2}{M_1}}$$

Rate of diffusion/effusion can be expressed as -

$$r = \frac{\text{volume diffused}}{\text{time taken}} \text{ or } \frac{\text{moles diffused}}{\text{time taken}} \text{ or } \frac{\text{pressure dropped}}{\text{time taken}}$$

$$\text{or } \frac{\text{distance travelled in horizontal tube of uniform cross-section}}{\text{time taken}}$$

$n_1$  moles  
+  
 $n_2$  moles

Effusing

**Ex.39** 32 ml of He effuses through a fine orifice in 1 minute. Then what volume of  $\text{CH}_4$  will diffuse in 1 minute under the similar condition.

**Sol.**

$$\therefore r \propto \frac{1}{\sqrt{M}}$$

$$r = \frac{\text{volume diffused}}{\text{time}}$$

$\therefore$  time is same so

$$\frac{V_{\text{CH}_4}}{V_{\text{He}}} = \sqrt{\frac{M_{\text{He}}}{M_{\text{CH}_4}}}$$

$$\frac{V_{\text{CH}_4}}{32} = \sqrt{\frac{4}{16}}$$

$$V_{\text{CH}_4} = \frac{1}{2} \times 32 = 16 \text{ mL}$$



**Ex.40** 20 dm<sup>3</sup> of Ne diffuse through a porous partition in 60 seconds. What volume of SO<sub>3</sub> will diffuse under similar conditions in 30 sec. (Atomic wt. of Ne = 20, S = 32)

**Sol.** 
$$\frac{r_{Ne}}{r_{SO_3}} = \sqrt{\frac{M_{SO_3}}{M_{Ne}}} \Rightarrow \frac{V_{Ne}/t_{Ne}}{V_{SO_3}/t_{SO_3}} = \sqrt{\frac{M_{SO_3}}{M_{Ne}}}$$

$$\Rightarrow V_{SO_3} = \frac{V_{Ne} \times t_{SO_3}}{t_{Ne}} \times \sqrt{\frac{M_{Ne}}{M_{SO_3}}} = \frac{20 \times 30}{60} \times \sqrt{\frac{20}{80}} = \frac{10}{2} = 5 \text{ dm}^3$$

**Ex.41** A gaseous mixture of O<sub>2</sub> and X containing 20% (mole %) of X, diffused through a small hole in 234 seconds while pure O<sub>2</sub> takes 224 seconds to diffuse through the same hole. Molecular weight of X is :

**Sol.** 
$$\frac{t_{mix}}{t_{O_2}} = \sqrt{\frac{M_{mix}}{M_{O_2}}}$$

$$\frac{234}{224} = \sqrt{\frac{M_{mix}}{32}}$$

$$\therefore M_{mix} = 34.921.$$

As the mixture contains 20% (mole %) of X, the molar ratio of O<sub>2</sub> and X may be represented as 0.8n : 0.2n, n being the total no. of moles.

$$\therefore M_{mix} = \frac{32 \times 0.8n + M_x \times 0.2n}{n} = 34.921$$

$$\therefore M_x (\text{mol. wt. of X}) = 46.6$$

**Ex.42** A mixture of H<sub>2</sub> and O<sub>2</sub> in 2 : 1 mole ratio is allowed to diffuse through a orifice. Calculate the composition of gases coming out initially.

**Sol.** 
$$\frac{r_1}{r_2} = \frac{n_1}{n_2} \sqrt{\frac{M_2}{M_1}}$$

where n<sub>1</sub> and n<sub>2</sub> are the moles of gases taken.

$$\frac{n'_1}{n'_2} = \frac{n_1}{n_2} \sqrt{\frac{M_2}{M_1}}$$

where n'<sub>1</sub> and n'<sub>2</sub> are the moles of gases diffused.

$$\frac{n'_1}{n'_2} = \frac{2}{1} \sqrt{\frac{32}{2}} = \frac{8}{1}$$

**Ex.43** One mole of nitrogen gas at 0.8 atm takes 38 s to diffuse through a pinhole, whereas one mole of an unknown compound of xenon with fluorine at 1.6 atm takes 57 s to diffuse through the same hole. Determine the molecular formula of the compound.

**Sol.** or  $\frac{r_2}{r_1} = \frac{p_2}{p_1} \left( \frac{M_1}{M_2} \right)^{1/2} \Rightarrow \frac{t_1}{t_2} = \left( \frac{p_2}{p_1} \right) \left( \frac{M_1}{M_2} \right)^{1/2}$

or  $M_2 = \left( \frac{p_2 t_2}{p_1 t_1} \right)^2 M_1$

$$M_2 = \left( \frac{1.6}{0.8} \times \frac{57}{38} \right)^2 \times 28 = 252 \text{ g mol}^{-1}$$

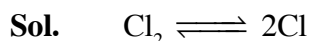
Let the molecular formula of the unknown compound be  $\text{XeF}_n$ .

$$M_{\text{Xe}} + nM_{\text{F}} = 252 \text{ or } 131 + 19n = 252$$

$$n = \frac{252 - 131}{19} = 6.36 \approx 6$$

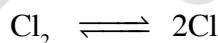
Hence, the molecular formula of the gas is  $\text{XeF}_6$ .

**Ex.44** At 1200°C, mixture of  $\text{Cl}_2$  and Cl atoms (both in gaseous state) effuses 1.16 times as fast as krypton effuses under identical conditions. Calculate the fraction of chlorine molecules dissociated into atoms.  $M(\text{Kr}) = 83.8 \text{ g mol}^{-1}$ .



$$\frac{r(\text{Cl}_2 \text{ and Cl mix})}{r(\text{Kr})} = 1.16 \sqrt{\frac{M(\text{Kr})}{M_{\text{av}}(\text{Cl}_2 + \text{Cl})}} = \sqrt{\frac{83.8}{M_{\text{av}}}}$$

$$\therefore M_{\text{av}} = \frac{83.8}{(1.16)^2} = 62.28 \text{ g mol}^{-1}$$



Initial mole                      1                      0

After dissociation            (1 - x)            2x

(x = degree of dissociation)

$$\text{Total moles after dissociation} = 1 - x + 2x = (1 + x)$$

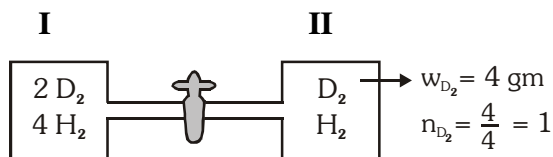
$$\therefore \frac{(1-x)M(\text{Cl}_2) + 2xM(\text{Cl})}{(1+x)} = 62.28 \Rightarrow \frac{(1-x) \times 71 + 2x \times 35.5}{1+x} = 62.28$$

$$x = 0.14$$

$$\therefore \% \text{ dissociation} = 14\%$$

**Ex.45** A mixture containing 2 moles of  $D_2$  and 4 moles of  $H_2$  is taken inside a container which is connected to another empty container through a nozzle. The nozzle is opened for certain time and then closed. The second bulb was found to contain 4 gm  $D_2$ . Then find % by moles of the lighter gases in second container.

**Sol.**



lighter gas =  $H_2$

$$\frac{r_{H_2}}{r_{D_2}} = \frac{n_{H_2}}{n_{D_2}} \sqrt{\frac{M_{D_2}}{M_{H_2}}} = \frac{n_{H_2}/t}{n_{D_2}/t}$$

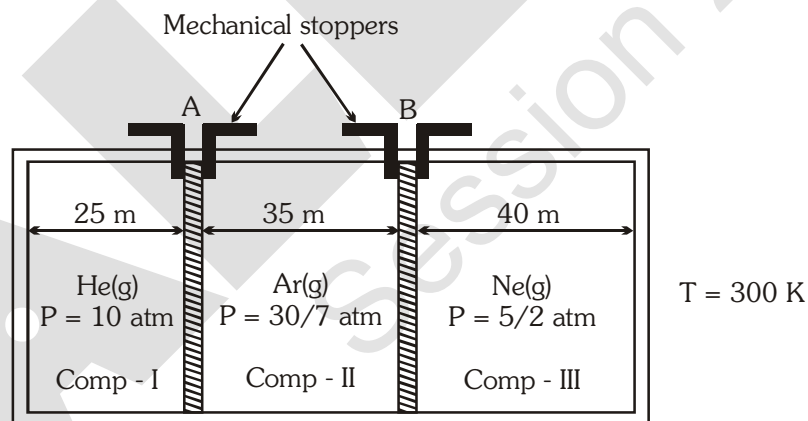
$$(\% \text{ mole of } H_2)_{II} = \left( \frac{n_{H_2}}{n_{H_2} + n_{D_2}} \right) \times 100$$

$$\therefore \frac{n_{H_2}}{n_{D_2}} \sqrt{\frac{M_{D_2}}{M_{H_2}}} = \frac{n_{H_2}}{n_{D_2}} \Rightarrow \frac{4}{2} \sqrt{\frac{4}{2}} = \frac{n_{H_2}}{1}$$

$$\Rightarrow n_{H_2} = 2\sqrt{2} \Rightarrow n_{D_2} = 1$$

$$(\% \text{ mole of } H_2)_{II} = \frac{(2\sqrt{2})}{(2\sqrt{2} + 1)} \times 100 = \frac{2 \times 1.44}{[(2 \times 1.44) + 1]} \times 100 = \frac{(2.8)}{(2.8 + 1)} \times 100 = \frac{(2.8)}{(2.8 + 1)} \times 100 = 73.87\%$$

**Ex.46** The figure shows **initial conditions** of a uniform cylinder with frictionless pistons A and B held in shown position by mechanical stoppers.

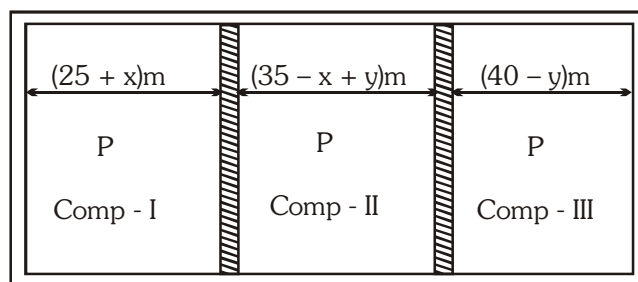


If the mechanical stoppers holding piston A and B as shown in figure are removed.

[Assume that temperature remains constant.]

- Pressure developed in each compartment in final state.
- What will be the final position of piston A (with respect to far left end of container)
- What will be the final position of piston B (with respect to far left end of container)

node06\B0AI-B0\Kota\JEE(Advanced)\Enthusias\Sheet\Module # Ideal gas, Solid state & Chemical Eq\Eng\01 Ideal gas\Theory.p65



$$P = 5 \text{ atm}$$

$x = 25 \text{ m}$

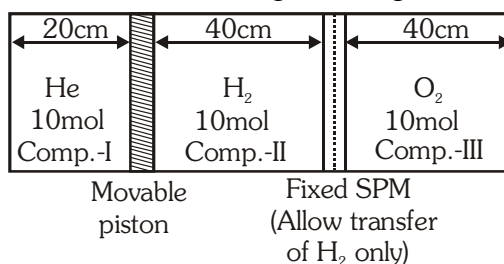
$$= (25 + x) = 25 + 25 = 50 \text{ m}$$

$$y = 20 \text{ m}$$

$$= (25 + x) + (35 - x + y) = 80m$$

**Ex.47** Few gases are filled in a container as shown in diagram and allowed to attain equilibrium. Then calculate the moles of  $H_2$  in compartment II.

(Assuming temperature remains constant through out the process.)



**Sol.** Piston move till pressure on both side becomes equal and  $H_2$  will pass in III compartment till pressure of  $H_2$  in II and III compartment becomes equal let the final position of containers as shown

For  $H_2$ :

$$(P_{H_2})_{II} = (P_{H_2})_{III}$$

$$\left(\frac{nRT}{V}\right)_{II} = \left(\frac{nRT}{V}\right)_{III}$$

$$\frac{x}{40-y} = \frac{10-x}{40} \quad \dots\dots\dots(i)$$

Finally total pressure of gases are equal

$$(P_T)_I = (P_T)_{II} = (P_T)_{III}$$

$$\frac{10}{20+y} = \frac{x}{40-y} = \frac{10-x}{40} \quad \dots\dots\dots(ii)$$

$$\frac{10}{20+y} = \frac{10-x}{40} \Rightarrow x = 10 - \frac{400}{20+y}$$

$$\frac{10}{20+y} = \frac{10 - \frac{400}{20+y}}{40-y}$$

$$400 - 10y = 10(20+y) - 400$$

$$400 - 10y = 200 + 10y - 400$$

$$600 = 20y \Rightarrow y = 30$$

$$x = 2$$

Moles of  $H_2$  in compartment II =  $x = 2$  mol

Moles of  $H_2$  in compartment II =  $10 - x = 8$  mol

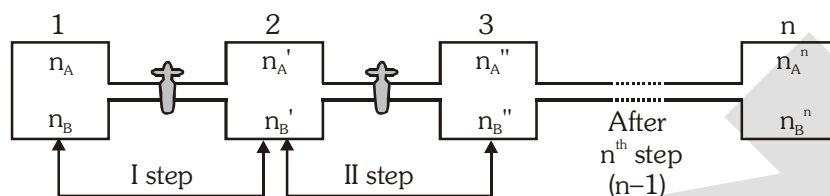
**Ex.48** Why a heavier gas from a gas mixture effuses at slower rates ?

**Sol.** In a gas mixture, the average kinetic energy of each gas  $\left(\frac{1}{2}mv^2\right)$  is the same  $\left(\frac{3}{2}RT\right)$ . Hence, heavier gas has smaller speed.

## 9.4 APPLICATION OF GRAHAM'S LAW OF DIFFUSION IN ENRICHMENT OF ISOTOPES

### ❖ Enrichment factor or Isotopic separation factor :

When two gases present in a container are allowed to diffuse in another container then gas having lower molecular mass will diffuse more and if this process is continued for large number of steps then we can obtain a mixture which is rich in a gas having lower molecular mass. Hence ultimately in the ultimate (last) container amount of lighter gas is larger as compared to heavier gas.



where,  $M_A > M_B$  [similar condition of T and V] &  $n_B^n \gg n_A^n$

Enrichment factor (f) is defined as the ratio of final ratio of moles in the mixture [after  $n^{\text{th}}$  step] with initial mole ratio of the mixture.

$$f = \frac{\left(\frac{n_A^n}{n_B^n}\right)}{\left(\frac{n_A}{n_B}\right)} = \left(\sqrt{\frac{M_B}{M_A}}\right)^n = \frac{\text{final molar ratio}}{\text{initial molar ratio}}$$

**Ex.49** A mixture of  $N_2$  and  $H_2$  has initially mass ratio of 196 : 1 then find after how many steps we can obtain a mixture containing 1 : 14 mole ratio of  $N_2$  and  $H_2$ .

**Sol.**

$$\begin{array}{cc} N_2 & H_2 \\ 196 & 1 \end{array}$$

$$\text{mole } \frac{196}{28} = 7 \quad \frac{1}{2}$$

$$\text{ratio } \frac{n_{N_2}}{n_{H_2}} = \frac{7}{\frac{1}{2}} = \frac{14}{1}$$

$$\frac{n_{N_2}}{n_{H_2}} = \frac{n_{N_2}}{n_{H_2}} \left(\sqrt{\frac{M_{H_2}}{M_{N_2}}}\right)^n = \frac{1}{14} = \frac{14}{1} \left(\sqrt{\frac{2}{28}}\right)^n, n = 4$$

**Ex.50** Find the ratio of moles of  $SO_2$  to  $CH_4$  after fifth diffusion steps if their initially mole ratio is 8 : 1.

**Sol.**

$$\frac{n_{SO_2}}{n_{CH_4}} = \frac{n_{SO_2}}{n_{CH_4}} \left(\sqrt{\frac{M_{CH_4}}{M_{SO_2}}}\right)^5$$

$$\frac{n_{SO_2}}{n_{CH_4}} = \frac{8}{1} \left(\sqrt{\frac{16}{64}}\right)^5 = \frac{n_{SO_2}}{n_{CH_4}} = \frac{1}{4}$$

## 10. KINETIC THEORY OF GASES

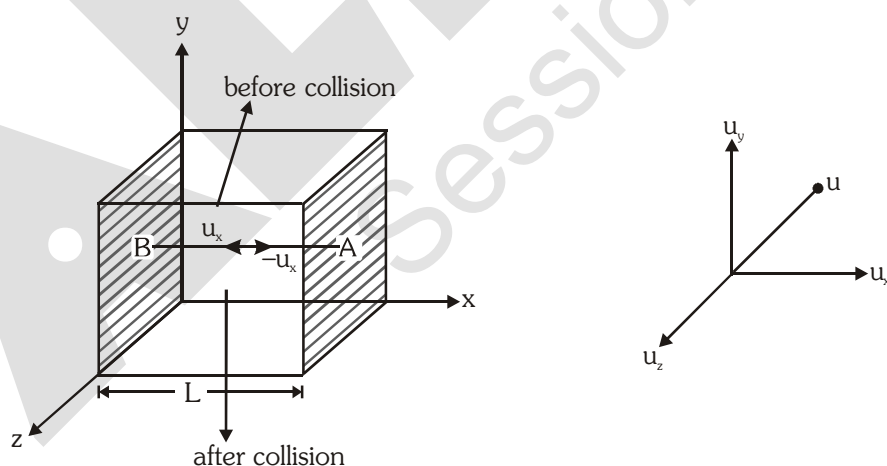
This is a theoretical model for ideal gas which can correlate the experimental facts (like Boyle's law, Charle's law & Avogadro's law etc.). It was presented by **Bernoulli in 1738** and developed in 1860 by **Clausius, Maxwell, Kroning and Boltzmann**. Postulates of kinetic theory of gases are :

- (i) All the gases consist of very small molecules or atoms whose volume is negligible compared to volume of container.
- (ii) There are no attractive or repulsive forces between the molecules.
- (iii) The gaseous molecules are under a continuous state of motion which is unaffected by gravity (the random straight line motion is known as brownian motion)
- (iv) Due to the continuous motion, collision between gaseous molecules and with the wall of container occurs. The collision with the wall of container are responsible for pressure exerted by the gas on the wall of container.
- (v) The molecule moves with different speed, however the speed of each molecule keep on changing as the collision occur.
- (vi) Collision among gas particles molecules is perfectly elastic, i.e., there is no loss in kinetic energy and moment during such collision.
- (vii) The average kinetic energy of gas particles will depends on absolute temperature only.

## 10.1 Kinetic gas equation :

Let us consider a cube of side  $L$ , that has  $N$  molecules each of mass  $m$  moving with velocity  $u$  in all direction and thus colliding with one each other and against sides of the container. Velocity  $u$  can be resolved into three components  $u_x$ ,  $u_y$  and  $u_z$  along there axis such that

$$u^2 = u_x^2 + u_y^2 + u_z^2$$



For a simplest case we consider motion of a molecule along x-axis only in which it moves towards face B with velocity  $u_x$ . After collision against face B it moves towards face A with velocity  $(-u_x)$  collision being elastic (which results in change in direction but not speed)

∴ Momentum before collision on face B =  $mu_x$

Momentum after collision on face B =  $-mu_x$

Change in momentum due to one collision on face B =  $mu_x - (-mu_x) = 2mu_x$

To strike face B again distance travelled =  $2L$

Time taken to strike face B again =  $\frac{2L}{u_x}$  seconds

$\therefore$  Number of collisions per second on face B along x-axis =  $\frac{u_x}{2L}$

$\therefore$  Rate of change in momentum due to  $\frac{u_x}{2L}$  collisions per second on face B along x-axis.

$$= 2mu_x \cdot \frac{u_x}{2L} = \frac{mu_x^2}{L}$$

Similarly for y-axis change in momentum per second =  $\frac{mu_y^2}{L}$  and for z-axis =  $\frac{mu_z^2}{L}$

Net force by N molecules on a wall,  $F_x = \frac{mu_{x_1}^2}{L} + \frac{mu_{x_2}^2}{L} + \dots + \frac{mu_{x_N}^2}{L} = \frac{M}{L} \cdot \Sigma u_x^2$

Now pressure =  $\frac{\text{Force}}{\text{Area of six faces}} = \frac{\frac{m}{L} \cdot \Sigma u_x^2}{L^2} = \frac{m \cdot \Sigma u_x^2}{L^3} = \frac{m \cdot \Sigma u^2}{V}$  [ $L^3 = \text{volume } V$ ]

$$\therefore PV = m \cdot \Sigma u_x^2$$

As  $\Sigma u_x^2 = \Sigma u_y^2 = \Sigma u_z^2$  and  $\Sigma u_x^2 + \Sigma u_y^2 + \Sigma u_z^2 = \Sigma u^2$

$$\therefore PV = m \cdot \Sigma u_x^2 = \frac{1}{3} m \cdot \Sigma u^2$$

$$PV = \frac{1}{3} m \left( \frac{u_1^2 + u_1^2 + \dots + u_N^2}{N} \right) \cdot N$$

$$\therefore PV = \frac{1}{3} mN u_{rms}^2$$

*This equation is called kinetic gas equation.*

## 10.2 Kinetic energy of gas molecules :

Total translational K.E. of molecules

$$= \frac{1}{2} mu_1^2 + \frac{1}{2} mu_2^2 + \dots + \frac{1}{2} m u_N^2 = \frac{1}{2} m \cdot \Sigma u^2 = \frac{1}{2} mN \cdot u_{rms}^2 = \frac{3}{2} PV = \frac{3}{2} nRT$$

$$\therefore \text{Average translational K.E. per mole} = \frac{3}{2} RT$$

$$\text{and (K.E.)}_{\text{per molecule}} = \frac{3}{2} \left( \frac{R}{N_A} \right) T = \frac{3}{2} kT$$

Where  $k = \text{Boltzman constant} = \frac{R}{N_A} = \frac{8.314 \text{ J/mol K}}{6.02 \times 10^{23}} = 1.3806 \times 10^{-23} \text{ J K}^{-1}$

- (K.E.)<sub>per molecule</sub> and (K.E.)<sub>per mol</sub> is only depend on absolute temperature. It is does not depend on the nature of gas. This conclusion is known as "*Maxwell's Generalisation*".



**Ex.51** Calculate the kinetic energy of 8 gram methane ( $\text{CH}_4$ ) at  $27^\circ\text{C}$  temperature.

**Sol.**  $n = \frac{8}{16} = \frac{1}{2}$ ,  $T = (27^\circ + 273) = 300 \text{ K}$ ,  $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

$$(\text{K.E.})_{\text{n mol}} = n \times \frac{3}{2} RT = \frac{1}{2} \times \frac{3}{2} \times 8.314 \times 300 = 1870.65 \text{ J}$$

**Ex.52** Calculate the pressure exerted by  $10^{23}$  gas molecules, each of mass  $10^{-25} \text{ kg}$ , in a container of volume  $1 \times 10^{-3} \text{ m}^3$  and having root mean square velocity of  $10^3 \text{ ms}^{-1}$ . Also calculate total kinetic energy and Temperature of the gas.

**Sol.** By kinetic theory

$$P = \frac{1}{3} \frac{mNu^2}{V} = \frac{1 \times 10^{-25} \times 10^{23} \times (10^3)^2}{3 \times 10^{-3}} = 3.33 \times 10^6 \text{ N m}^{-2}$$

$$\text{Total KE} = \left( \frac{1}{2} mu_{\text{rms}}^2 \right) \times N = \frac{1}{2} \times 10^{-25} \times (10^3)^2 \times 10^{23} = \frac{1}{2} \times 10^4 = 0.5 \times 10^4 \text{ J}$$

$$\text{Also total KE} = \frac{3}{2} nRT, \text{ where } n (\text{mole}) = \frac{10^{23}}{N_A} = \frac{10^{23}}{6.023 \times 10^{23}}$$

$$0.5 \times 10^4 = \frac{3}{2} \times \frac{10^{23}}{6.023 \times 10^{23}} \times 8.314 \times T$$

$$\therefore T = \frac{0.5 \times 10^4 \times 2 \times 6.023}{3 \times 8.314} = 2415 \text{ K}$$

### 10.3 Root Mean Square Velocity ( $u_{\text{rms}}$ ) by kinetic gas equation :

$$PV = \frac{1}{3} mN u_{\text{rms}}^2$$

$$\therefore u_{\text{rms}} = \sqrt{\frac{3PV}{mN}} = \sqrt{\frac{3P}{d}} = \sqrt{\frac{3RT}{M}}$$

### 10.4 Different kind of speed of molecules :

$$(i) \text{ Average or mean speed, } u_{\text{av}} = \frac{u_1 + u_2 + \dots + u_N}{N} = \sqrt{\frac{8RT}{\pi M}}$$

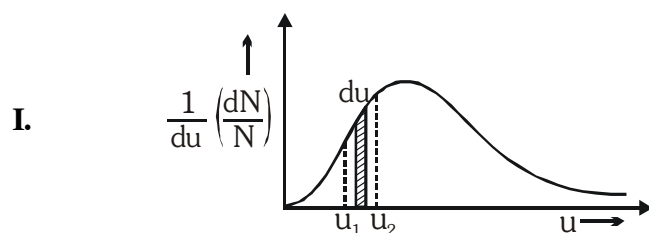
$$(ii) \text{ Root mean square speed, } u_{\text{rms}} = \sqrt{\frac{u_1^2 + u_2^2 + \dots + u_N^2}{N}} = \sqrt{\frac{3RT}{M}}$$

$$(iii) \text{ Most probable speed, } u_{\text{mp}} = \sqrt{\frac{2RT}{M}}$$

It is the speed at which maximum fraction of molecules are travelling

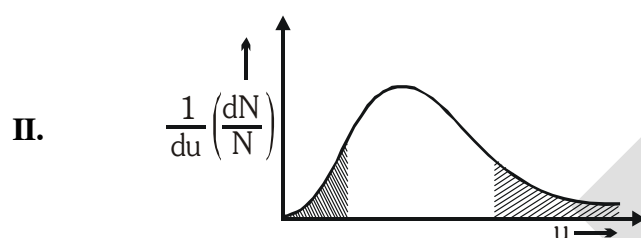


## 11.1 Properties of Maxwell's graph :

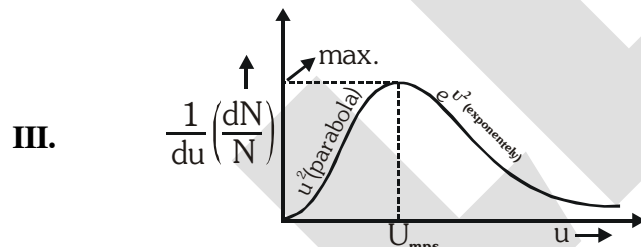


$$\text{Area between } u_1 \text{ and } u_2 = \int_{u_1}^{u_2} \frac{1}{du} \left( \frac{dN}{N} \right) du = \int_{u_1}^{u_2} \left( \frac{dN}{N} \right)$$

Hence, total fraction of particles with speed between  $u_1$  and  $u_2$   
= Area under the curve represents fraction of molecules.

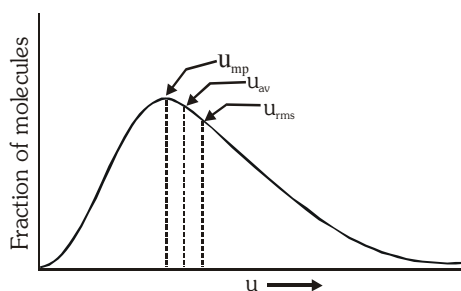


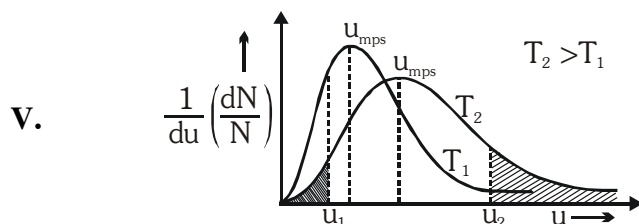
It can be seen from the above figure, that the fraction of molecules having either very low speeds or very high speeds are small in numbers.



The curve at any temperature is parabolic near the origin, since the factor  $u^2$  is dominant in this region, the exponential function being approximately equal to unity. At high values of  $u$ , however, the exponential factor dominates the behaviour of the function, causing it to decrease rapidly in value. As a consequence of the contrasting behaviour of two factors, the product function passes through a maximum at a speed known as the most probable speed ( $u_{mps}$ ). Thus, the most probable speed is the speed possessed by the maximum fraction of the molecules.

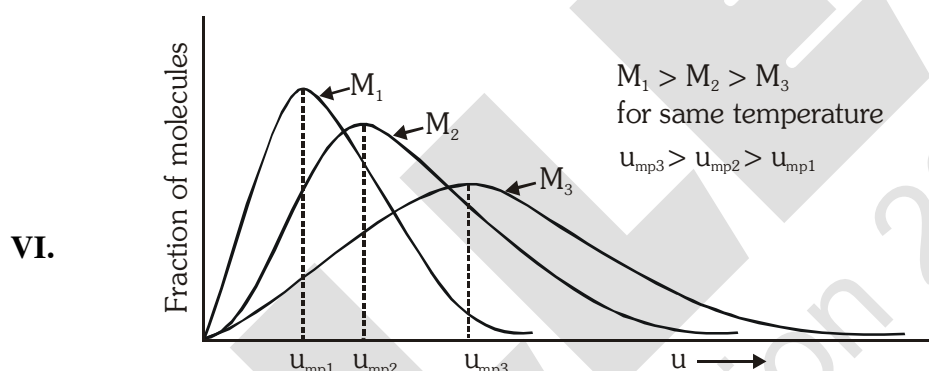
## IV Graph between fraction of molecules vs molecular speeds :





Total area under the curve will be constant and will be unity at all temperatures. The above figure illustrates the distribution of speeds at two temperatures  $T_1$  and  $T_2$ . Since the total no. of molecules is same at both temperatures, increase in the K.E. of the molecules results decrease in fraction of molecules having lower speed range and increase in fraction of molecules having higher speed range on increasing the temperature.

On increasing temperature the value of  $u_{mps}$  (most probable speed) will increase. Also the curve at the higher temperature  $T_2$  has its  $u_{mps}$  shifted to a higher value compared with that for  $T_1$ , whereas corresponding fraction of molecules has decreased. But at the same time, the curve near  $u_{mps}$  has become broader at the higher temperature indicating the more molecules possess speeds near to most probable speed.

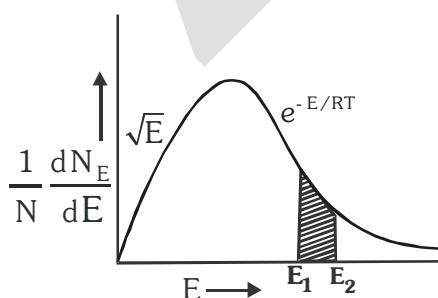


At a given temperature  $u_{mps}$  will be more for lighter gas ( $M_3$ ) but fraction of molecules moving with  $u_{mps}$  will be more for heavier gas ( $M_1$ ).

**Note :** Effect of  $M$  and  $T$  are opposite.

## 11.2 Maxwell Distribution of kinetic energy :

**By Maxwell equation :**  $dN = 4\pi N \left( \frac{M}{2\pi RT} \right)^{3/2} \cdot e^{-\frac{Mu^2}{2RT}} u^2 \cdot du = 2\pi \left( \frac{1}{\pi RT} \right)^{3/2} \sqrt{E} \cdot e^{-E/RT} \cdot dE$



The shaded area of this graph indicate the fraction of particles having energy between  $E_1$  and  $E_2$

**Ex.53** Four particles have speed 2, 3, 4 and 5 cm/s respectively. Find their avg. & rms speed :

**Sol.**  $U_{\text{avg.}} = \frac{U_1 + U_2 + U_3 + \dots + U_N}{N}$

$$U_{\text{avg.}} = \frac{2 + 3 + 4 + 5}{4} = 3.5 \text{ cm/s}$$

$$U_{\text{r.m.s.}} = \sqrt{\frac{U_1^2 + U_2^2 + U_3^2 + \dots}{N}}$$

$$u_{\text{rms}} = \sqrt{\frac{2^2 + 3^2 + 4^2 + 5^2}{4}} = \frac{\sqrt{54}}{2} \text{ cm/s}$$

**Ex.54** At what temperature do the average speed of  $\text{CH}_4$  molecule equal the average speed of  $\text{O}_2$  molecule at 300 K ?

**Sol.**  $(U_{\text{avg}})_{\text{CH}_4} = (U_{\text{avg}})_{\text{O}_2}$

$$\sqrt{\frac{8RT}{\pi \times 16}} = \sqrt{\frac{8 \times R \times 300}{\pi \times 32}}$$

$$T = 150 \text{ K}$$

**Ex.55** At 27°C find the ratio of root mean square speeds of ozone to oxygen :-

**Sol.**  $\frac{U_{\text{rms}}(\text{O}_3)}{U_{\text{rms}}(\text{O}_2)} = \sqrt{\frac{\frac{3RT}{M.W_{\text{O}_3}}}{\frac{3RT}{M.W_{\text{O}_2}}}} = \sqrt{\frac{M.W_{\text{O}_2}}{M.W_{\text{O}_3}}} = \sqrt{\frac{32}{48}} = \sqrt{\frac{2}{3}}$

**Ex.56** The temperature at which  $U_{\text{rms}}$  of He becomes equal to  $U_{\text{mp}}$  of  $\text{CH}_4$  at 500 K.

**Sol.**  $(U_{\text{rms}})_{\text{He}} = (U_{\text{mp}})_{\text{CH}_4}$

$$\sqrt{\frac{3RT_{\text{He}}}{M_{\text{He}}}} = \sqrt{\frac{2RT_{\text{CH}_4}}{M_{\text{CH}_4}}}$$

$$\frac{3T}{4} = \frac{2 \times 500}{16}$$

$$T = \frac{250}{3} \text{ K}$$

**Ex.57** Calculate the root mean square speed of  $\text{H}_2$  molecules under following condition.

- 2 mole of  $\text{H}_2$  at 27°C.
- 3 mole of  $\text{H}_2$  in a 5 lit container at  $10^5$  Pa.
- 4 mole of  $\text{H}_2$  at the density of 1 gm/ml at  $10^5$  Pa.

**Sol.** (a)  $U_{r.m.s.} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \text{ J/mol K} \times 300 \text{ K}}{2 \times 10^{-3} \text{ kg}}} = 1934.24 \text{ m/sec.}$

(b)  $U_{r.m.s.} = \sqrt{\frac{3PV}{nM}} = \sqrt{\frac{3 \times 10^5 \text{ Pa} \times 5 \times 10^{-3} \text{ m}^3}{3 \text{ mol} \times 2 \times 10^{-3} \text{ kg}}} = 500 \text{ m/sec.}$

(c)  $U_{r.m.s.} = \sqrt{\frac{3P}{d}} = \sqrt{\frac{3 \times 10^5 \text{ Pa}}{10^3 \text{ kg/m}^3}} = 17.32 \text{ m/sec.}$

**Ex.58** Calculate the fraction of  $N_2$  molecules at 1 atm and  $27^\circ\text{C}$  whose speeds are in the range of  $(U_{mp} - 0.005 U_{mp})$  to  $(U_{mp} + 0.005 U_{mp})$ ?

**Sol.** Most probable speed,

$$U_{mp} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2 \times 8.314 \times 300}{28 \times 10^{-3}}} = 422.09 \text{ m/sec}$$

$$\begin{aligned} du &= (U_{mp} + 0.005 U_{mp}) - (U_{mp} - 0.005 U_{mp}) \\ &= 2 \times 0.005 \times U_{mp} = 4.22 \text{ m/sec} \end{aligned}$$

From Maxwell's equation :

$$\frac{dN}{N} = 4\pi \left[ \frac{M}{2\pi RT} \right]^{\frac{3}{2}} e^{-\frac{MU_{mp}^2}{2RT}} U_{mp}^2 du$$

$$\frac{dN}{N} = 4\pi \left( \frac{M}{2\pi RT} \right)^{\frac{3}{2}} \cdot e^{-\frac{M}{2RT} \times \frac{2RT}{M}} \cdot U_{mp}^2 \cdot du$$

$$\frac{dN}{N} = 4 \times 3.14 \times \left( \frac{28 \times 10^{-3}}{2 \times 3.14 \times 8.314 \times 300} \right)^{\frac{3}{2}} e^{-1} \times (422.09)^2 \times 4.22$$

$$\frac{dN}{N} = 8.3 \times 10^{-3}$$

**Ex.59** Calculate the fraction of  $N_2$  molecules whose speeds are in the range of  $U_{mp}$  to  $(U_{mp} + f \times U_{mp})$ ?

**Sol.**  $\frac{dN}{N} = 4\pi \left[ \frac{M}{2\pi RT} \right]^{\frac{3}{2}} e^{-\frac{MU^2}{2RT}} U^2 du$

Here,  $U = U_{mp} = \sqrt{\frac{2RT}{M}}$ ,  $du = f \times U_{mp}$

$$\Rightarrow \frac{dN}{N} = 4\pi \left[ \frac{M}{2\pi RT} \right]^{\frac{3}{2}} e^{-\frac{M}{2RT} \times \frac{2RT}{M}} \times \frac{2RT}{M} \times f \times \left( \frac{2RT}{M} \right)^{\frac{1}{2}}$$

$$\frac{dN}{N} = 4\pi \times \frac{1}{\pi\sqrt{\pi}} e^{-1} \times f = \frac{4f}{e\sqrt{\pi}}$$

This fraction does not depend upon  $U_{mp}$ , or Temperature and depends only on 'f' factor.

- (i) Therefore, we can conclude that at two different temperatures the fraction of molecules between  $U_{mp1}$  to  $(U_{mp1} + f \times U_{mp1})$  and between  $U_{mp2}$  to  $(U_{mp2} + f \times U_{mp2})$  are same.
- (ii) Even for two different gases say  $N_2$  and  $O_2$ , the fraction of molecules between  $U_{mp}$  to  $(U_{mp} + f \times U_{mp})$  are same.

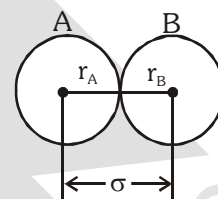
## 12. COLLISION PARAMETERS :

### Assumption :

All the particles (molecules or atoms) have rigid, similar shape and size and are spherical in nature that will not change after collision.

- 12.1 Collision diameter :** It is the closest distance between the centres of two molecules taking part in collision.

Collision diameter ( $\sigma$ ) =  $r_A + r_B$



### 12.2 Collision Frequency :

It is the total number of molecular collisions taking place per second per unit volume of the gas. The no. of collisions made by a single molecule with other molecules per unit time (**collision number**) are given by

$$Z_1 = \sqrt{2} \pi \sigma^2 U_{avg} N^*$$

The total number of bimolecular collision per unit time is given as  $Z_{11}$  (**collision frequency**)

$$Z_{11} = \frac{1}{2} (Z_1 N^*) = \frac{1}{2} \times N^* \times \sqrt{2} \pi \sigma^2 U_{avg} N^*$$

$$Z_{11} = \frac{1}{\sqrt{2}} \pi \sigma^2 U_{avg} N^{*2}$$

- (f) If the collisions involve two unlike molecules, the no. of bimolecular collision is given as  $Z_{12}$ .

$$Z_{12} = \pi \sigma_{12}^2 \left( \frac{8kT}{\pi \mu} \right)^{\frac{1}{2}} N_1^* N_2^*$$

Where  $N_1^*$  and  $N_2^*$  are the no. of molecules per unit volume of the two types of gases,  $\sigma_{12}$

is the average diameter of two molecules, that is  $\sigma_{12} = \frac{\sigma_1 + \sigma_2}{2}$  &  $\mu$  is the reduced mass,

that is  $\mu = \frac{m_1 m_2}{(m_1 + m_2)}$ ,  $m_1$  &  $m_2$  are the mass of single molecule respectively 1 and 2.

### 12.3 Mean free path :

The mean free path is the average distance travelled by a molecule between two successive collisions. We can express it as follows :

$$\lambda = \frac{\text{Average distance travelled per unit time}}{\text{No. of collisions made by single molecule per unit time}}$$

$$= \frac{U_{avg}}{Z_1} = \frac{U_{avg}}{\sqrt{2} \pi \sigma^2 U_{avg} N^*} = \frac{1}{\sqrt{2} \pi \sigma^2 N^*}$$

### 12.4 Wall collision :

It represents the total number of molecules colliding at the wall per unit area per unit time.

$$Z_w = \frac{1}{4} N^* \cdot u_{av} = \frac{P \cdot N_A}{\sqrt{2\pi MRT}}$$

### 12.5 Rate of effusion :

If the cross-section area of orifice in the vessel is 'A', then the number of molecules effusing out per unit time is

$$r_{eff.} = Z_w \cdot A = \frac{P \cdot N_A \cdot A}{\sqrt{2\pi MRT}}$$

**Ex.60.** Calculate  $\lambda$ ,  $Z_1$  and  $Z_{11}$  for oxygen at 298 K and  $10^{-3}$  mm Hg. Given  $\sigma = 3.61 \times 10^{-8}$  cm.

**Sol.**  $N^* = \frac{P}{kT} = \frac{10^{-3} \times 101325}{760 \times 1.38 \times 10^{-23} \times 298} = 0.324 \times 10^{20}$

$$U_{avg} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8}{3.14} \times \frac{8.314 \times 298}{32 \times 10^{-3}}} = 444.138 \text{ m/sec}$$

$$Z_1 = \sqrt{2} \pi \sigma^2 U_{avg} N^* = \sqrt{2} \times 3.14 \times (3.61 \times 10^{-10})^2 \times 444.138 \times 0.324 \times 10^{20} \\ = 8.326 \times 10^3 \text{ sec}^{-1}$$

$$Z_{11} = \frac{1}{2} Z_1 N^* = \frac{1}{2} \times 8.326 \times 10^3 \text{ sec}^{-1} \times 0.324 \times 10^{20} = 13.488 \times 10^{22} \text{ m}^{-3} \text{ sec}^{-1};$$

$$\lambda = \frac{U_{avg.}}{Z_1} = \frac{444.138 \text{ m/sec}}{8.326 \times 10^3 \text{ sec}^{-1}} = 5.334 \times 10^{-2} \text{ m}$$

**Ex.61** Two flask A and B have equal volume. A is maintained at 300 K and B at 600 K while A contains  $H_2$  gas, B has an equal mass of  $CH_4$  gas. Assuming ideal behaviour for both the gases, find the following.

- Flask containing greater number of moles
- Flask in which pressure is greater
- Flask in which  $U_{avg}$  of the molecules are greater
- Flask with greater mean free path of molecules (Collision diameters of  $H_2$  &  $CH_4$  may be taken same)
- Flask with greater molar kinetic energy.
- Flask in which the total kinetic energy is greater
- Flask in which  $Z_1$  and  $Z_{11}$  are greater

**Sol.**

|            |             |
|------------|-------------|
| A<br>$H_2$ | B<br>$CH_4$ |
| 300K       | 600K        |

(a)  $N_{H_2} = \frac{m}{2} N_A$  ;  $N_{CH_4} = \frac{m}{16} N_A$

$\therefore$  molecules of  $H_2$  in flask A > molecules of  $CH_4$  in flask B



$$(b) \quad P_A V = n_A R T_A \quad ; \quad P_B V = n_B R T_B$$

$$\Rightarrow \quad \frac{P_A}{P_B} = \frac{n_A T_A}{n_B T_B} = \frac{m/2}{m/16} \times \frac{300}{600} = 4$$

$\therefore$  pressure of  $H_2$  in flask A > pressure of  $CH_4$  in flask B

$$(c) \quad (U_{avg})_A = \sqrt{\frac{8 R T_A}{\pi M_A}} \quad ; \quad (U_{avg})_B = \sqrt{\frac{8 R T_B}{\pi M_B}}$$

$$\frac{(U_{avg})_A}{(U_{avg})_B} = \sqrt{\frac{T_A}{T_B} \times \frac{M_B}{M_A}} = \sqrt{\frac{300}{600} \times \frac{16}{2}} = 2$$

$\therefore$   $U_{avg}$  of  $H_2$  in flask A >  $U_{avg}$  of  $CH_4$  in flask B

$$(d) \quad \lambda = \frac{1}{\sqrt{2\pi\sigma^2 N^*}} = \frac{1}{\sqrt{2\pi\sigma^2 \times P}} \times kT \quad [\text{where } N^* = P/kT]$$

$$\frac{\lambda_A}{\lambda_B} = \frac{T_A}{T_B} \times \frac{P_B}{P_A} = \frac{300}{600} \times \frac{1}{4} = \frac{1}{8}$$

$\therefore \quad \lambda_B > \lambda_A$

$$(e) \quad \text{molar K.E.} = \frac{3}{2} RT$$

$$\therefore \quad T_B > T_A$$

$\therefore$  KE of  $CH_4$  in flask B > KE of  $H_2$  in flask A

$$(f) \quad (KE)_{total} = \frac{3}{2} RT \times n$$

$$\frac{(KE)_{T,A}}{(KE)_{T,B}} = \frac{(300 \times \frac{m}{2})}{(600 \times \frac{m}{16})} = \frac{1}{2} \times 8 = 4$$

$\therefore \quad (KE)_{T,A} > (KE)_{T,B}$

$$(g) \quad (i) \quad Z_1 = \sqrt{2\pi\sigma^2} U_{avg} N^*$$

$$\frac{(Z_1)_A}{(Z_1)_B} = \frac{(U_{avg})_A}{(U_{avg})_B} \times \frac{N_A^*}{N_B^*} = 2 \times \frac{N_A}{N_B} = 2 \times 8 = 16$$

$\therefore \quad (Z_1)_A > (Z_1)_B \quad (Z_1)_A > (Z_1)_B$

$$(ii) \quad Z_{11} = \frac{1}{\sqrt{2}} \pi \sigma^2 U_{avg} N^{*2}$$

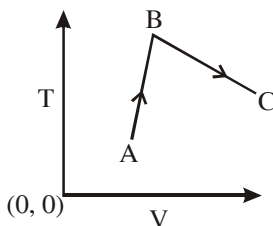
$$\frac{(Z_{11})_A}{(Z_{11})_B} = \frac{(U_{avg})_A}{(U_{avg})_B} \times \frac{(N_A^*)^2}{(N_B^*)^2} = 2 \times \frac{N_A}{N_B} = 2 \times 8^2 = 128$$

$\therefore \quad (Z_{11})_A > (Z_{11})_B$

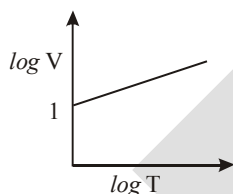
EXERCISE # O-I

Single Correct :

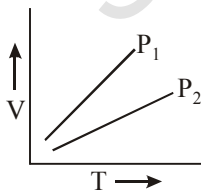
1. In the given isobaric process shown by graph between T & V.



- (A) Moles decreases throughout  
(B) Moles first increases then decreases  
(C) Moles first decreases then increases  
(D) Moles cannot be predicted from given data
2. At constant pressure of 0.821 atm ;  $\log V$  vs  $\log T$  is plotted as shown in-  
Then number of moles present in experiment -



- (A) 1 (B) 10 (C) 100 (D) 0.1
3. A gas at a pressure of 5.0 atm is heated from  $0^\circ\text{C}$  to  $546^\circ\text{C}$  and simultaneously compressed to one-third of its original volume. Hence final pressure is  
(A) 10 atm (B) 30 atm (C) 45 atm (D) 5 atm
4. A flask containing air (open to the atmosphere) is heated from 300 K to 500 K. Then % of air escaped to the atmosphere is -  
(A) 20.0 (B) 40 (C) 60 (D) 80
5. 10 g of a gas at 1 atm, 273 K occupies 5 litres. The temp. at which the volume becomes double for the same mass of gas at the same pressure is ?  
(A) 273K (B)  $-273^\circ\text{C}$  (C)  $273^\circ\text{C}$  (D)  $546^\circ\text{C}$
6. A gas is found to have a formula  $[\text{CO}]_x$ . If its vapour density is 70 the value of x is  
(A) 2.5 (B) 3.0 (C) 5.0 (D) 6.0
7. V versus T curves at constant pressure  $P_1$  and  $P_2$  for an ideal gas are shown in Fig. Which is correct



- (A)  $P_1 > P_2$  (B)  $P_1 < P_2$  (C)  $P_1 = P_2$  (D) All
8. A container when is empty weighs 50 gm. After certain liquid of density  $25 \text{ gm/dm}^3$  is filled its mass becomes equal to 100 gm. The volume of the container will be :  
(A)  $0.25 \text{ dm}^3$  (B)  $0.5 \text{ dm}^3$  (C)  $1 \text{ dm}^3$  (D)  $2 \text{ dm}^3$
9. A vessel contains mono atomic 'He' at 1 bar and 300 K, determine its number density -  
(A)  $2.4 \times 10^{25} \text{ m}^{-3}$  (B)  $6.8 \times 10^{23} \text{ m}^{-3}$  (C)  $4.8 \times 10^{26} \text{ m}^{-3}$  (D)  $9.2 \times 10^{27} \text{ m}^{-3}$

10. A rigid container containing 10 gm gas at some pressure and temperature. The gas has been allowed to escape from the container due to which pressure of the gas becomes half of its initial pressure and temperature become  $(2/3)^{\text{rd}}$  of its initial. The mass of gas (in gms) escaped is  
 (A) 7.5 (B) 1.5 (C) 2.5 (D) 3.5
11. The density of gas A is twice that of B at the same temperature the molecular weight of gas B is thrice that of A. The ratio of pressure of gas A and gas B will be  
 (A) 1 : 6 (B) 7 : 8 (C) 6 : 1 (D) 1 : 4
12. In a rigid container  $\text{NH}_3$  is kept at certain temperature, if on doubling the temperature it is completely dissociated into  $\text{N}_2$  and  $\text{H}_2$ . Find final pressure to initial pressure ratio :  
 (A) 4 (B) 2 (C)  $\frac{1}{2}$  (D)  $\frac{1}{4}$
13. Gas A (1 mol) dissociates in a closed rigid container of volume 0.16 lit. as per following reaction.  
 $2\text{A (g)} \longrightarrow 3\text{B (g)} + 2\text{C (g)}$   
 If degree of dissociation of A is 0.4 and remains constant in entire range of temperature, then the correct P vs T graph is [Given  $R = 0.08 \text{ lit-atm/mol/K}$ ]
- (A)

(B)

(C)

(D)
14. A gaseous reaction,  
 $3\text{A} \longrightarrow 2\text{B}$   
 is carried out in a 0.0821 litre closed container initially containing 1 mole of gas A. After sufficient time a curve of P (atm) vs T (K) is plotted and the angle with x-axis was found to be  $42.95^\circ$ . The degree of association of gas A is [Given :  $\tan 42.95 = 0.8$ ]  
 (A) 0.4 (B) 0.6 (C) 0.5 (D) 0.8
15. 4.0 g of argon has pressure P and temperature T K in a vessel. On keeping the vessel at  $50^\circ$  higher temperature, 0.8 g of argon was given out to maintain the pressure P. The original temperature was :  
 (A) 73 K (B) 100 K (C) 200 K (D) 510 K
16. The total pressure exerted by a number nonreacting gases is equal to the sum of partial pressure of the gases under the same conditions is known as :  
 (A) Boyle's law (B) Charle's law (C) Avogadro's law (D) Dalton's law
17. Dalton's law cannot be applied for which gaseous mixture at normal temperatures:  
 (A)  $\text{O}_2$  and  $\text{N}_2$  (B)  $\text{NH}_3$  and  $\text{HCl}$  (C) He and  $\text{N}_2$  (D)  $\text{CO}_2$  and  $\text{O}_2$
18. A closed vessel contains helium and ozone at a pressure of P atm. The ratio of He and oxygen atoms is 1 : 1. If helium is removed from the vessel, the pressure of the system will reduce to :  
 (A) 0.5 P atm (B) 0.75 P atm (C) 0.25 P atm (D) 0.33 P atm
19. At constant temperature  $200 \text{ cm}^3$  of  $\text{N}_2$  at 720 mm and  $400 \text{ cm}^3$  of  $\text{O}_2$  at 750 mm pressure are put together in a one litre flask. The final pressure of mixture is  
 (A) 111 mm (B) 222 mm (C) 333 mm (D) 444 mm
20. If saturated vapours are compressed slowly (temperature remaining constant) to half the initial volume, the vapour pressure will :  
 (A) Become four times (B) become doubled (C) Remain unchanged (D) Become half

21. A box of 1L capacity is divided into two equal compartments by a thin partition which are filled with 2g H<sub>2</sub> and 16g CH<sub>4</sub> respectively. The pressure in each compartment is recorded as P atm. The total pressure when partition is removed will be :  
(A) P (B) 2P (C) P/2 (D) P/4
22. A vessel has N<sub>2</sub> gas and water vapours at a total pressure of 1 atm. The vapour pressure of water is 0.3 atm. The contents of this vessel are transferred to another vessel having one third of the capacity of original volume, completely at the same temperature the total pressure of this system in the new vessel is -  
(A) 3.0 atm (B) 1 atm (C) 3.33 atm (D) 2.4 atm
23. Which gas effuses fastest under identical conditions -  
(A) N<sub>2</sub> (B) O<sub>2</sub> (C) Cl<sub>2</sub> (D) CH<sub>4</sub>
24. The rate of diffusion of methane at a given temperature is twice that of a gas X. The molecular weight of X is:  
(A) 64 (B) 32 (C) 4.0 (D) 8.0
25. The rate of diffusion of two gases A and B is in the ratio of 1 : 4 and that of B and C in the ratio of 1 : 3 the rate of diffusion of C with respect to A is -  
(A)  $\frac{1}{12}$  (B) 12 (C) 6 (D) 4
26. A gas X diffuses three times faster than another gas Y the ratio of their densities i.e., D<sub>x</sub> : D<sub>y</sub> is  
(A) 1/3 (B) 1/9 (C) 1/6 (D) 1/12
27. Rate of diffusion of a gas is :  
(A) directly proportional to its density  
(B) directly proportional to its molecular weight  
(C) directly proportional to the square of its molecular weight  
(D) inversely proportional to the square root of its molecular weight
28. Since the atomic weights of carbon nitrogen and oxygen are 12, 14 and 16 respectively, among the following pairs of gases, the pair that will diffuse at the same rate is :  
(A) CO<sub>2</sub> and N<sub>2</sub>O (B) CO<sub>2</sub> and N<sub>2</sub>O<sub>3</sub>  
(C) CO<sub>2</sub> and CO (D) CO<sub>2</sub> and NO
29. If the four tubes of a car are filled to the same pressure with N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub> and He separately then which one will be filled first :  
(A) N<sub>2</sub> (B) O<sub>2</sub> (C) H<sub>2</sub> (D) He
30. The increasing order of effusion among the gases, H<sub>2</sub>, O<sub>2</sub>, NH<sub>3</sub> and CO<sub>2</sub> is -  
(A) H<sub>2</sub>, CO<sub>2</sub>, NH<sub>3</sub>, O<sub>2</sub> (B) H<sub>2</sub>, NH<sub>3</sub>, O<sub>2</sub>, CO<sub>2</sub>  
(C) H<sub>2</sub>, O<sub>2</sub>, NH<sub>3</sub>, CO<sub>2</sub> (D) CO<sub>2</sub>, O<sub>2</sub>, NH<sub>3</sub>, H<sub>2</sub>
31. The rate of diffusion of hydrogen is about-  
(A)  $\frac{1}{2}$  that of Helium (B) 1.4 times that of Helium  
(C) twice that of H (D) Four times that of Helium
32. Under identical conditions of pressure and temperature. 4 L of gaseous mixture (H<sub>2</sub> and CH<sub>4</sub>) effuses through a hole in 5min whereas 4 L of a gas X of molecular mass 36 takes to 10 min to effuse through the same hole. The mole ratio of H<sub>2</sub> : CH<sub>4</sub>, in the mixture is -  
(A) 1 : 2 (B) 2 : 1 (C) 2 : 3 (D) 1 : 1



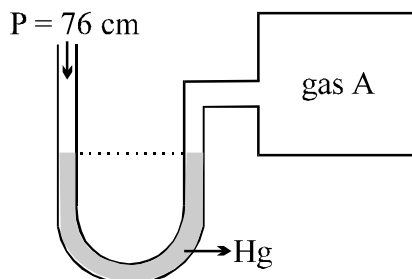
43. At STP, the order of root mean square speed of molecules  $H_2$ ,  $N_2$ ,  $O_2$  and  $HBr$  is :  
 (A)  $H_2 > N_2 > O_2 > HBr$  (B)  $HBr > O_2 > N_2 > H_2$   
 (C)  $HBr > H_2 > O_2 > N_2$  (D)  $N_2 > O_2 > H_2 > HBr$
44. Four particles have speed 2, 3, 4 and 5 cm/s respectively. Their rms speed is :  
 (A) 3.5 cm/s (B)  $\left(\frac{27}{2}\right)$  cm/s (C)  $\sqrt{54}$  cm/s (D)  $\left(\frac{\sqrt{54}}{2}\right)$  cm/s
45. A flask has 10 molecules out of which four molecules are moving at  $7\text{ms}^{-1}$  & the remaining are moving at same speed of  $X\text{ms}^{-1}$ . If Urms of the gas is  $5\text{ms}^{-1}$ . The value of 'X' will be  
 (A) 5 (B) 3 (C) 9 (D) 16
46. If the average velocity of  $N_2$  molecules is 0.3 m/sec. at  $27^\circ\text{C}$ , then the velocity of 0.6 m/sec will take place at :  
 (A) 273 K (B) 927 K (C) 1000 K (D) 1200 K
47. Which of the following expression does not give root mean square velocity –  
 (A)  $\left(\frac{3RT}{M_w}\right)^{\frac{1}{2}}$  (B)  $\left(\frac{3P}{DM_w}\right)^{\frac{1}{2}}$  (C)  $\left(\frac{3P}{D}\right)^{\frac{1}{2}}$  (D)  $\left(\frac{3PV}{nM_w}\right)^{\frac{1}{2}}$
48. Which one of the following gases would have the highest R.M.S. velocity at  $25^\circ\text{C}$  ?  
 (A) Oxygen (B) Carbon dioxide (C) Sulphur dioxide (D) Carbon monoxide
49. At what temperature would the rms speed of a gas molecule have twice its value at  $100^\circ\text{C}$  ?  
 (A) 4192 K (B) 1492 K (C) 9142 K (D) 2491 K
50. Two flasks X and Y have capacity 1L and 2L respectively and each of them contains 1 mole of a gas. The temperature of the flask are so adjusted that average speed of molecules in X is twice as those in Y. The pressure in flask X would be  
 (A) same as that in Y (B) half of that in Y (C) twice of that in Y (D) 8 times of that in Y
51. Temperature at which most probable speed of  $O_2$  becomes equal to root mean square speed of  $N_2$  is [Given :  $N_2$  at  $427^\circ\text{C}$ ]  
 (A) 732 K (B) 1200 K (C) 927 K (D) 800 K
52. The density ratio of  $O_2$  and  $H_2$  is 16 : 1. The ratio of their  $U_{\text{rms}}$  is :-  
 (A) 4 : 1 (B) 16 : 1 (C) 1 : 4 (D) 1 : 16
53. Which of the gas have highest fraction of molecules at  $27^\circ\text{C}$  in most probable speed region -  
 (A)  $H_2$  (B)  $N_2$  (C)  $O_2$  (D)  $CO_2$
54. The av. K.E./mole of an ideal monoatomic gas at  $27^\circ\text{C}$  is  
 (A) 900 cal (B) 1800 cal (C) 300 cal (D) None
55. The average kinetic energy of an ideal gas per molecule in SI units at  $25^\circ\text{C}$  will be :  
 (A)  $6.17 \times 10^{-21}$  kJ (B)  $6.17 \times 10^{-21}$  J (C)  $6.17 \times 10^{-20}$  J (D)  $7.16 \times 10^{-20}$  J

56. At what temperature will be total kinetic energy (KE) of 0.30 mole of He be the same as the total KE of 0.40 mole of Ar at 400 K :  
(A) 400 K (B) 373 K (C) 533 K (D) 300 K
57. Average K.E. of  $\text{CO}_2$  at  $27^\circ\text{C}$  is E. The average kinetic energy of  $\text{N}_2$  at the same temperature will be  
(A) E (B) 22E (C) E/22 (D)  $E/\sqrt{2}$
58. If a gas expands at constant temperature then :  
(A) No. of gaseous molecule decreases (B) kinetic energy of molecule decreases  
(C) K.E. remain same (D) K.E. increases
59. Total translational kinetic energy possessed by 8 gm methane at  $273^\circ\text{C}$   
(R = 2 Cal/mol-K)  
(A) 819 calorie (B) 409.5 calorie (C) 1638 calorie (D) None of these
60. Ideal gas equation in terms of K.E. per unit volume E, is-  
(A)  $P = \frac{3}{2}RT$  (B)  $P = \frac{2}{3}E$  (C)  $P = \frac{2}{3}RT$  (D)  $P = \frac{3}{2}RT$
61. Three gases A, B and C are at same temperature. If their r.m.s. speed are in the ratio  $1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}}$  then their molar masses will be in the ratio :  
(A) 1 : 2 : 3 (B) 3 : 2 : 1 (C)  $1 : \sqrt{2} : \sqrt{3}$  (D)  $\sqrt{3} : \sqrt{2} : 1$
62. The following gases are present under similar condition of T, P & V. The longest mean free path stands for  
(A)  $\text{H}_2$  (B)  $\text{N}_2$  (C)  $\text{O}_2$  (D)  $\text{Cl}_2$
63. At constant volume,  $Z_{11}$  is directly proportional to -  
(A)  $\sqrt{P}$  (B) P (C)  $T^2$  (D) T
64. At constant pressure,  $Z_{11}$  is directly proportional to -  
(A)  $\sqrt{T}$  (B)  $\frac{1}{T}$  (C)  $\frac{1}{\sqrt{T}}$  (D)  $\frac{1}{T^{3/2}}$
65. On increasing the temperature of an ideal gas at constant volume, the mean free path -  
(A) Increases  
(B) Decreases  
(C) Remains unchanged  
(D) May or may not change depending on the size of gas molecules

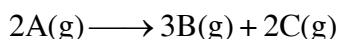
EXERCISE # O-II

One or more may be correct :

1. An open ended mercury manometer is used to measure the pressure exerted by a trapped gas as shown in the figure. Initially manometer shows no difference in mercury level in both columns as shown in diagram.

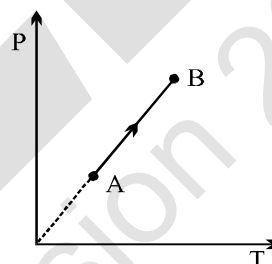


After sparking 'A' dissociates according to following reaction

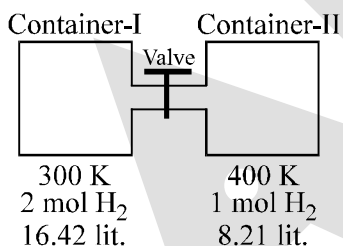


If pressure of Gas "A" decreases to 0.8 atm. Then (Assume temperature to be constant and is 300 K)

- (A) total pressure increased by 1.3 atm
  - (B) total pressure increased by 0.3 atm
  - (C) total pressure increased by 22.3 cm of Hg
  - (D) difference in mercury level is 228 mm.
2. Select the correct option for an ideal gas undergoing a process as shown in diagram.
    - (A) If 'n' is changing, 'V' must also be changing.
    - (B) If 'n' is constant, 'V' must be constant.
    - (C) If 'n' is constant, 'V' must be changing.
    - (D) If 'n' is changing, 'V' must be constant.



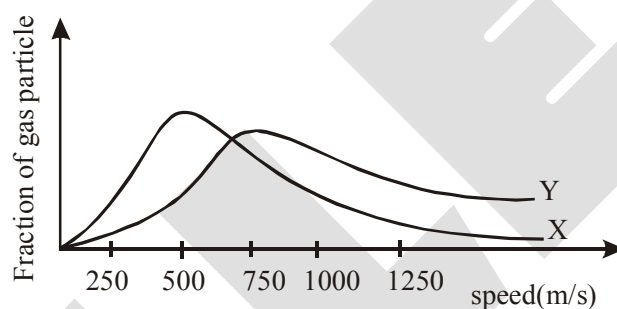
3. Select the correct option(s):



- (A) Pressure in container-I is 3 atm before opening the valve.
  - (B) Pressure after opening the valve is 3.57 atm.
  - (C) Moles in each compartment are same after opening the valve.
  - (D) Pressure in each compartment are same after opening the valve.
4. When an equimolar mixture of two gases A and B [ $M_A > M_B$ ] is allowed to effuse through a Pin hole select incorrect statement -
    - (A) B comes out at a faster rate
    - (B) Relative rate of effusion of A increases with time
    - (C) Rate of effusion of B will always be greater
    - (D) Initially, with equal molar ratio rate of effusion of B is greater than rate of effusion of A.

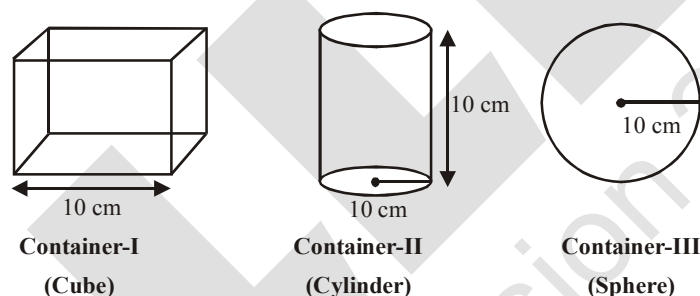


5. Select the correct option(s) for an ideal gas
- (A) Most probable speed increases with increase in temperature
- (B) Fraction of particles moving with most probable speed increases with increase in temperature
- (C) Fraction of particles moving with most probable speed are more for  $\text{Cl}_2$  than  $\text{H}_2$  under similar condition of T, P & V.
- (D) Most probable speed is more for  $\text{Cl}_2$  than  $\text{H}_2$  at same temperature
6. A closed vessel at temperature T contain a mixture of two diatomic gases A and B. Molar mass of A is 16 times that of B and mass of gas A contained in the vessel is 2 times that of B. Which of the following statements are correct-
- (A) Average kinetic energy per molecule of A is equal to that of B.
- (B) Root mean square velocity of B is four times that of A
- (C) Pressure exerted by B is eight time of that exerted by A
- (D) Number of molecules of B, in the cylinder, is eight time that of A
7. The graph below shows the distribution of molecular speed of two ideal gases X and Y at 200K. on the basis of the below graph identify the correct statements -



- (A) If gas X is methane, then gas Y can be  $\text{CO}_2$
- (B) Fraction of molecules of X must be greater than Y in a particular range of speed at 200K
- (C) Under identical conditions rate of effusion of Y is greater than that of X
- (D) The molar kinetic energy of gas X at 200K is equal to the molar kinetic energy of Y at 200K
8. Identify the correct statements when a fixed amount of ideal gas is heated in a container fitted with a movable piston always operating at constant pressure.
- (A) Average distance travelled between successive collisions will decreases.
- (B) Collisions frequency increases since speed of the molecules increases with increase in temperature.
- (C) Average relative speed of approach remains unaffected.
- (D) Average angle of approach remains unaffected.
9. Choose the correct statement(s) among the following
- (A) Average molecular speed of gases increases with decrease in fraction of molecules moving slowly
- (B) Rate of effusion of gases increases with increase in collision frequency at constant volume.
- (C) Rate of effusion is inversely proportional to molecular weight of gas
- (D) Mean free path does not change with change in temperature at constant pressure.
10. Which of the following quantities is the same for all ideal gases at the same temperature :
- (A) The kinetic energy of 1 mol
- (B) The kinetic energy of 1 g
- (C) The number of molecules in 1 mol
- (D) The number of molecules in 1 g

11. Choose the correct statement(s) among the following -
  - (A) The mean free path ( $\lambda$ ) of gaseous molecules is directly proportional to temperature of gas at constant volume
  - (B) The mean free path ( $\lambda$ ) of gaseous molecules is inversely proportional to pressure of gas at constant volume
  - (C) The mean free path ( $\lambda$ ) of gaseous molecules is directly proportional to volume of gas at constant T
  - (D) The mean free path ( $\lambda$ ) of gaseous molecules is directly proportional to volume of gas at constant P
12. Which statement is/are correct for postulates of kinetics theory of gases -
  - (A) Gases are composed of molecules whose size is negligible compared with the average distance between them
  - (B) Molecules moves randomly in straight lines in all directions and at various speeds.
  - (C) When molecules collide with one another the collisions are elastic. In an elastic collision the loss of kinetic energy takes place
  - (D) The average kinetic energy of a molecule is proportional to the absolute temperature.
13. Three closed containers are filled with equal amount of same ideal gas.



If pressure is same in all container then -

- (A)  $(U_{\text{rms}})_3 > (U_{\text{rms}})_2 > (U_{\text{rms}})_1$       (B)  $(U_{\text{rms}})_3 = (U_{\text{rms}})_2 = (U_{\text{rms}})_1$   
 (C)  $\lambda_1 < \lambda_2 < \lambda_3$  ( $\lambda \rightarrow$  Mean free path)      (D)  $(z_1)_1 < (z_1)_2 < (z_1)_3$

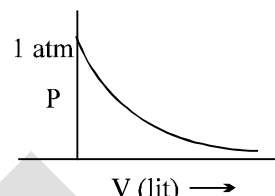
14. Which of the following statements is (are) true -
- (A) The ratio of the average speed to the rms speed is independent of the temperature
  - (B) The square of the mean squared speed of the molecule is equal to the mean square speed at a certain temperature
  - (C) Mean kinetic energy of the gas molecules at any given temperature is independent of the mean speed
  - (D) The difference between rms speed and average speed at any temperature for different gases diminished as larger molar masses are considered

## Paragraph for Q.15 &amp; 17

Question No. 18 to 20 are based on the following Passage. Read it carefully & answer the questions that follow

On the recently discovered 10<sup>th</sup> planet it has been found that the gases follow the relationship  $PV^{1/2} = nCT$  where C is constant other notation are as usual (V in lit., P in atm and T in Kelvin). A curve is plotted

between P and V at 500 K & 2 moles of gas as shown in figure



15. The value of constant C is  
 (A) 0.01 (B) 0.001 (C) 0.005 (D) 0.002
16. Find the slope of the curve plotted between P Vs T for closed container of volume 2 lit. having same moles of gas  
 (A)  $\frac{e}{2000}$  (B) 2000 e (C) 500 e (D)  $\frac{2}{1000e}$
17. If a closed container of volume 200 lit. of O<sub>2</sub> gas (ideal gas) at 1 atm & 200 K is taken to planet. Find the pressure of oxygen gas at the planet at 821 K in same container  
 (A)  $\frac{10}{e^{100}}$  (B)  $\frac{20}{e^{50}}$  (C) 1 atm (D) 2 atm

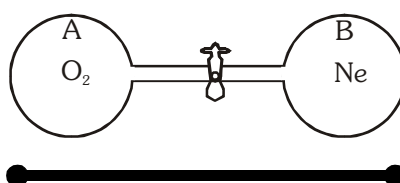
## Paragraph for Question 18 to 20

The constant motion and high velocities of gas particles lead to some important practical consequences. One such consequence is that as minimum rapidly when they come in contact. The mixing of different gases by random molecular motion and with frequent collisions is called diffusion. A similar process in which gas molecules escape through a tiny hole into a vacuum is called effusion.

18. Helium gas at 1 atm and SO<sub>2</sub> at 2 atm pressure, temperature being the same, are released separately at the same moment into 1 m long evacuated tubes of equal diameters. If helium reaches the other end of the tube in t sec, what distance SO<sub>2</sub> would traverse in the same time interval in the other tube ?  
 (A) 25 cm (B) 50 cm (C) 60 cm (D) 75 cm
19. 4 g of H<sub>2</sub> effused through a pinhole in 10 sec at constant temperature and pressure. The amount of oxygen effused in the same time interval and at the same conditions of temperature and pressure would be :  
 (A) 4 g (B) 8 g (C) 16 g (D) 32 g
20. For 10 min. each at 27°C, from two identical bulbs helium and an unknown gas X at equal pressures are leaked into a common vessel of 3 L capacity. The resulting pressure is 4.1 atm and the mixture contains 0.4 mol of helium. The molar mass of gas X is :  
 (A) 16 (B) 32 (C) 64 (D) None of these

## Paragraph for Question 21 to 22

Initially, flask A contained oxygen gas at 27°C and 950 mm of Hg, and flask B contained neon gas at 27°C and 900 mm. Finally, the two flasks were joined by means of a narrow tube of negligible volume equipped with a stopcork and gases were allowed to mix up freely. The final pressure in the combined system was found to be 910 mm of Hg.



21. What is the correct relationship between volumes of the two flasks ?  
 (A)  $V_B = 3V_A$  (B)  $V_B = 4V_A$  (C)  $V_B = 5V_A$  (D)  $V_B = 4.5V_A$
22. How many moles of gas are present in flask A in the final condition, if volume of flask B is 304 litre ? ( $R = 0.08 \text{ atm L mol}^{-1} \text{ K}^{-1}$ )  
 (A) 7.58 (B) 3.79 (C) 15.16 (D) None of these

**TABLE TYPE QUESTION :**

| Column-I<br>(Gases at different conditions)   | Column-II<br>(Value of speed (m/s)) | Column-III                                |
|-----------------------------------------------|-------------------------------------|-------------------------------------------|
| (A) $\text{CH}_4$ at $27^\circ\text{C}$       | (P) $U_{\text{rms}} = 342.5$        | (I) Molar K.E. = 3750 Joule               |
| (B) $\text{SO}_2$ at $27^\circ\text{C}$       | (Q) $U_{\text{mp}} = 1100$          | (II) Molar K.E. = 5000 Joule              |
| (C) 4 gm He at 1 atm and 24.6 litre           | (R) $U_{\text{rms}} = 685$          | (III) Average K.E. per gram = 937.5 Joule |
| (D) 32 gm $\text{O}_2$ at $127^\circ\text{C}$ | (S) $U_{\text{rms}} = 550$          | (IV) Average K.E. per gram = 234 Joule.   |

(Given :  $R = \frac{25}{3} \frac{\text{J}}{\text{mol} \times \text{K}}$ ,  $\sqrt{30} = 5.48$ ,  $\sqrt{\frac{2}{3}} = 0.8$ ,  $\sqrt{5} = 2.2$ )

23. Which of the following is correct  
(A) A ; R ; 4                      (B) A ; R ; 2                      (C) A ; Q ; 4                      (D) B ; R ; 1
24. Which of the following is correct  
(A) B ; Q ; 1                      (B) B ; Q ; 2                      (C) B ; P ; 1                      (D) C ; S ; 3
25. Which of the following is correct  
(A) C ; Q ; 3                      (B) D ; R ; 2                      (C) D ; S ; 1                      (D) D ; S ; 4

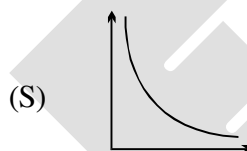
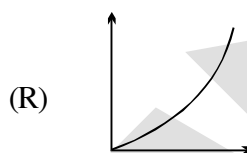
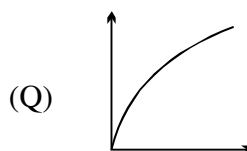
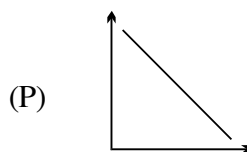
Match the column :

26. Match the entries in column I with entries in Column II and then pick out correct options.

Column I

(A)  $\frac{1}{V^2}$  vs P for ideal gas at constant T and n.(B)  $V$  vs  $\frac{1}{T}$  for ideal gas at constant P and n(C)  $\log P$  vs  $\log V$  for ideal gas at constant T and n.(D)  $V$  vs  $\frac{1}{P^2}$  for ideal gas at constant T and n.

Column II



27. Match the column-

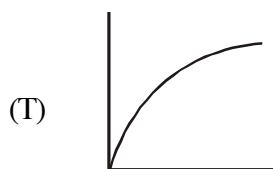
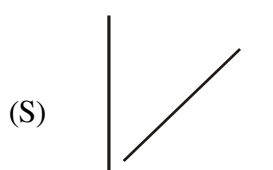
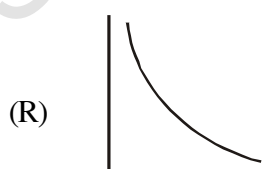
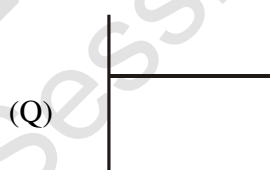
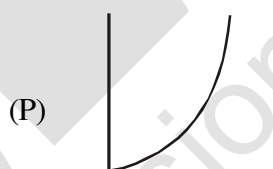
Column-I

(For an ideal gas at constant pressure)

(A)  $V$  v/s  $T$ (B)  $TV$  v/s  $\left(\frac{1}{T^2}\right)$ (C)  $\frac{V}{T}$  v/s  $V$ (D)  $TV$  v/s  $T$ 

Column-II

(correct graph)

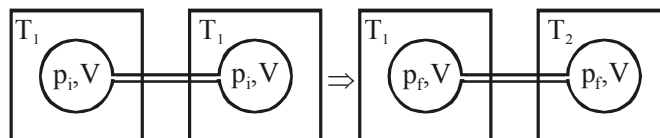


JEE-MAINS

1. According to the kinetic theory of gases, in an ideal gas, between two successive collisions a gas molecule travels - [AIEEE-2003]
  - (1) In a straight line path
  - (2) with an accelerated velocity
  - (3) In a circular path
  - (4) In a wavy path
2. What volume of hydrogen gas, at 273K and 1 atm, pressure will be consumed in obtaining 21.6g of elemental boron (atomic mass = 10.8) from the reduction of boron trichloride by hydrogen ? [AIEEE-2003]
  - (1) 44.8 L
  - (2) 22.4 L
  - (3) 89.6 L
  - (4) 67.2 L
3. As the temperature is raised from 20°C to 40°C, the average kinetic energy of neon atoms changes by factor of which of the following ? [AIEEE-2004]
  - (1) 1/2
  - (2)  $\sqrt{(313/293)}$
  - (3) 313/293
  - (4) 2
4. Equal masses of methane and oxygen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by oxygen is - [AIEEE-2008]
  - (1) 2/3
  - (2)  $\frac{1}{3} \times \frac{273}{298}$
  - (3)  $\frac{1}{3}$
  - (4)  $\frac{1}{2}$
5. The molecular velocity of any gas is :- [AIEEE-2011]
  - (1) inversely proportional to the square root of temperature
  - (2) inversely proportional to absolute temperature
  - (3) directly proportional to square of temperature
  - (4) directly proportional to square root of temperature
6.  $\alpha$ ,  $v$  and  $u$  represent most probable velocity, average velocity and root mean square velocity respectively of a gas at a particular temperature. The correct order among the following is - [JEE(Main)-2012]
  - (1)  $\alpha > u > v$
  - (2)  $v > u > \alpha$
  - (3)  $u > v > \alpha$
  - (4)  $u > \alpha > v$
7. An open vessel at 300 K is heated till  $\frac{2}{5}$ th of the air in it is expelled. Assuming that the volume of the vessel remains constant, the temperature to which the vessel is heated is :- [JEE(Main-online)-2012]
  - (1) 750 K
  - (2) 400 K
  - (3) 500 K
  - (4) 1500K
8. For 1 mol of an ideal gas at constant temperature T, the plot of (log P) against (log V) is a (P : Pressure, V : Volume) :- [JEE(Main-online)-2012]
  - (1) Straight line parallel to x-axis
  - (2) Curve starting at origin
  - (3) Straight line with a negative slope
  - (4) Straight line passing through origin
9. The relationship among most probable velocity, average velocity and root mean square velocity is respectively :- [JEE(Main-online)-2012]
  - (1)  $\sqrt{2} : \sqrt{8/\pi} : \sqrt{3}$
  - (2)  $\sqrt{2} : \sqrt{3} : \sqrt{8/\pi}$
  - (3)  $\sqrt{3} : \sqrt{8/\pi} : \sqrt{2}$
  - (4)  $\sqrt{8/\pi} : \sqrt{3} : \sqrt{2}$
10. Which one of the following is the wrong assumption of kinetic theory of gases? [JEE(Main-online)-2013]
  - (1) All the molecules move in straight line between collision and with same velocity.
  - (2) Molecules are separated by great distances compared to their sizes.
  - (3) Pressure is the result of elastic collision of molecules with the container's wall.
  - (4) Momentum and energy always remain conserved.

11. By how many folds the temperature of a gas would increase when the root mean square velocity of the gas molecules in a container of fixed volume is increased from  $5 \times 10^4$  cm/s to  $10 \times 10^4$  cm/s ?  
[JEE(Main-online)-2013]
- (1) Four (2) three (3) Two (4) Six
12. For gaseous state, if most probable speed is denoted by  $C$ , average speed by  $\bar{C}$  and mean square speed by  $C$ , then for a large number of molecules the ratios of these speeds are :-  
[JEE(Main-offline)-2013]
- (1)  $C : \bar{C} : C = 1.225 : 1.128 : 1$  (2)  $C : \bar{C} : C = 1.128 : 1.225 : 1$   
(3)  $C : \bar{C} : C = 1 : 1.128 : 1.225$  (4)  $C : \bar{C} : C = 1 : 1.225 : 1.128$
13. A gaseous compound of nitrogen and hydrogen contains 12.5% (by mass) of hydrogen. The density of the compound relative to hydrogen is 16. The molecular formula of the compound is :  
[JEE(Main-online)-2014]
- (1)  $\text{NH}_2$  (2)  $\text{NH}_3$  (3)  $\text{N}_3\text{H}$  (4)  $\text{N}_2\text{H}_4$
14. The initial volume of a gas cylinder is 750.0 mL. If the pressure of gas inside the cylinder changes from 840.0 mm Hg to 360.0 mm Hg, the final volume the gas will be  
[JEE(Main-online)-2014]
- (1) 1.750 L (2) 7.50 L (3) 3.60 L (4) 4.032 L
15. The temperature at which oxygen molecules have the same root mean square speed as helium atoms have at 300 K is :  
[JEE(Main-online)-2014]
- (Atomic masses : He = 4 u, O = 16 u)
- (1) 1200 K (2) 600 K (3) 300 K (4) 2400 K
16. Which of the following is not an assumption of the kinetic theory of gases ?  
[JEE-Mains (online)-2015]
- (1) Gas particles have negligible volume.  
(2) A gas consists of many identical particles which are in continual motion.  
(3) At high pressure, gas particles are difficult to compress.  
(4) Collisions of gas particles are perfectly elastic.

17. Two closed bulbs of equal volume ( $V$ ) containing an ideal gas initially at pressure  $p_i$  and temperature  $T_1$  are connected through a narrow tube of negligible volume as shown in the figure below. The temperature of one of the bulbs is then raised to  $T_2$ . The final pressure  $p_f$  is :- **[JEE-Mains-2016]**



- (1)  $2p_i \left( \frac{T_1 T_2}{T_1 + T_2} \right)$       (2)  $p_i \left( \frac{T_1 T_2}{T_1 + T_2} \right)$       (3)  $2p_i \left( \frac{T_1}{T_1 + T_2} \right)$       (4)  $2p_i \left( \frac{T_2}{T_1 + T_2} \right)$
18. At 300 K, the density of a certain gaseous molecule at 2 bar is double to that of dinitrogen ( $N_2$ ) at 4 bar. The molar mass of gaseous molecule is:- **[JEE-Mains-2017(ONLINE)]**
- (1) 28 g mol<sup>-1</sup>      (2) 56 g mol<sup>-1</sup>      (3) 224 g mol<sup>-1</sup>      (4) 112 g mol<sup>-1</sup>
19. Assuming ideal gas behaviour, the ratio of density of ammonia to that of hydrogen chloride at same temperature and pressure is : **[JEE-Mains-2018(ONLINE)]**
- (Atomic wt. of Cl = 35.5 u)
- (1) 0.64      (2) 1.64      (3) 1.46      (4) 0.46



## JEE-ADVANCED

- Calculate the total pressure in a 10 litre cylinder which contains 0.4 g He, 1.6 g oxygen and 1.4 g of nitrogen at 27°C. Also calculate the partial pressure of He gas in the cylinder. Assume ideal behaviour for gases. [JEE 1997]
- According to Graham's law, at a given temperature the ratio of the rates of diffusion  $\frac{r_A}{r_B}$  of gases A and B is given by : [JEE 1998]
 

(A)  $\frac{P_A}{P_B} \left( \frac{M_A}{M_B} \right)^{1/2}$  (B)  $\left( \frac{M_A}{M_B} \right) \left( \frac{P_A}{P_B} \right)^{1/2}$  (C)  $\frac{P_A}{P_B} \left( \frac{M_B}{M_A} \right)^{1/2}$  (D)  $\frac{M_A}{M_B} \left( \frac{P_B}{P_A} \right)^{1/2}$
- An evacuated glass vessel weighs 50.0 g when empty, 148.0 gm when filled with a liquid of density 0.98 g/mL and 50.5 g when filled with an ideal gas at 760 mm Hg at 300 K. Determine the molecular weight of the gas. [JEE 1998]
- The pressure exerted by 12 g of an ideal gas at temperature  $t^\circ\text{C}$  in a vessel of volume  $V$  is one atm. When the temperature is increased by 10 degrees at the same volume, the pressure increases by 10 %. Calculate the temperature 't' and volume 'V'. [molecular weight of gas = 120] [JEE 1999]
- One mole of  $\text{N}_2$  gas at 0.8 atm takes 38 sec to diffuse through a pin hole, whereas one mole of an unknown compound of Xenon with F at 1.6 atm takes 57 sec to diffuse through the same hole. Calculate the molecular formula of the compound. (At. wt. Xe = 138, F = 19) [JEE 1999]
- The r.m.s. velocity of hydrogen is  $\sqrt{7}$  times the r.m.s. velocity of nitrogen. If  $T$  is the temperature of the gas : [JEE 2000]
 

(A)  $T(\text{H}_2) = T(\text{N}_2)$  (B)  $T(\text{H}_2) > T(\text{N}_2)$  (C)  $T(\text{H}_2) < T(\text{N}_2)$  (D)  $T(\text{H}_2) = \sqrt{7} T(\text{N}_2)$
- Statement-1 :** The pressure of a fixed amount of an ideal gas is proportional to its temperature.  
**Statement-2 :** Frequency of collision and their impact both increase in proportion to the square root of temperature. True/False. [JEE 2000]
- The root mean square velocity of an ideal gas at constant pressure varies with density as  
 (A)  $d^2$  (B)  $d$  (C)  $d^{1/2}$  (D)  $1/d^{1/2}$  [JEE 2001]
- Which one of the following  $V, T$  plots represents the behaviour of one mole of an ideal gas at one atm? [JEE 2002]
 

(A)

(B)

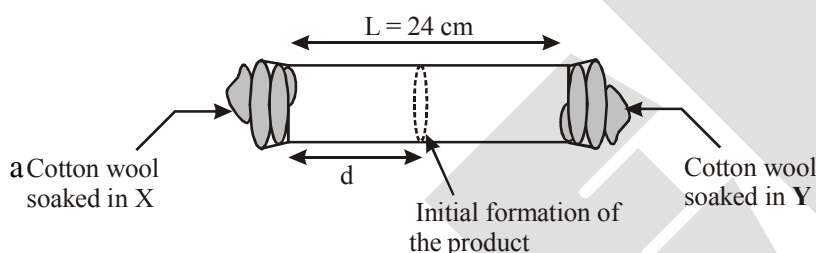
(C)

(D)
- The average velocity of gas molecules is 400 m/sec. Calculate its (rms) velocity at the same temperature. [JEE 2003]
- The ratio of the rate of diffusion of helium and methane under identical condition of pressure and temperature will be  
 (A) 4 (B) 2 (C) 1 (D) 0.5 [JEE 2005]

12. At 400 K, the root mean square (rms) speed of a gas X (molecular weight = 40) is equal to the most probable speed of gas Y at 60 K. The molecular weight of the gas Y is [JEE 2009]
13. To an evacuated vessel with movable piston under external pressure of 1 atm., 0.1 mol of He and 1.0 mol of an unknown compound (vapour pressure 0.68 atm. at 0°C) are introduced. Considering the ideal gas behaviour, the total volume (in litre) of the gases at 0°C is close to [JEE 2011]

**Paragraph for Question 14 & 15**

X and Y are two volatile liquids with molar weights of  $10\text{g mol}^{-1}$  and  $40\text{g mol}^{-1}$  respectively. Two cotton plugs, one soaked in X and the other soaked in Y, are simultaneously placed at the ends of a tube of length  $L = 24\text{ cm}$ , as shown in the figure. The tube is filled with an inert gas at 1 atmosphere pressure and a temperature of 300K. Vapours of X and Y react to form a product which is first observed at a distance  $d\text{ cm}$  from the plug soaked in X. Take X and Y to have equal molecular diameters and assume ideal behaviour for the inert gas and the two vapours. [JEE 2014]



14. The value of  $d$  in cm (shown in the figure), as estimated from Graham's law, is -  
 (A) 8 (B) 12 (C) 16 (D) 20
15. The experimental value of  $d$  is found to be smaller than the estimate obtained using Graham's law. This is due to -  
 (A) Larger mean free path for X as compared to that of Y  
 (B) Larger mean free path for Y as compared to that of X  
 (C) Increased collision frequency of Y with the inert gas as compared to that of X with the inert gas  
 (D) Increased collision frequency of X with the inert gas as compared to that of Y with the inert gas
16. A closed tank has two compartments A and B, both filled with oxygen (assumed to be ideal gas). The partition separating the two compartments is fixed and is a perfect heat insulator (Figure 1). If the old partition is replaced by a new partition which can slide and conduct heat but does NOT allow the gas to leak across (Figure 2), the volume (in  $\text{m}^3$ ) of the compartment A after the system attains equilibrium is \_\_\_\_\_. [JEE 2018]

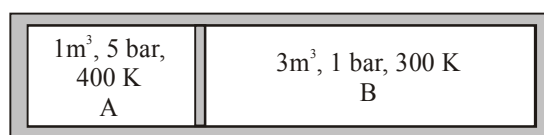


Figure 1

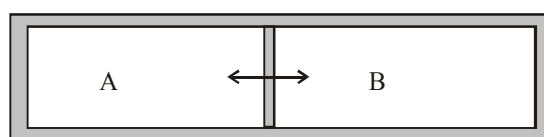


Figure 2

## ANSWER KEY

## EXERCISE - O-I

|     |          |     |          |     |          |     |          |
|-----|----------|-----|----------|-----|----------|-----|----------|
| 1.  | Ans (C)  | 2.  | Ans (C)  | 3.  | Ans. (C) | 4.  | Ans. (B) |
| 5.  | Ans.(C)  | 6.  | Ans.(C)  | 7.  | Ans.(B)  | 8.  | Ans. (D) |
| 9.  | Ans.(A)  | 10. | Ans.(C)  | 11. | Ans.(C)  | 12. | Ans. (A) |
| 13. | Ans.(B)  | 14. | Ans.(B)  | 15. | Ans. (C) | 16. | Ans.(D)  |
| 17. | Ans.(B)  | 18. | Ans. (C) | 19. | Ans.(D)  | 20. | Ans.(C)  |
| 21. | Ans.(A)  | 22. | Ans(D)   | 23. | Ans.(D)  | 24. | Ans.(A)  |
| 25. | Ans(B)   | 26. | Ans.(B)  | 27. | Ans.(D)  | 28. | Ans.(A)  |
| 29. | Ans.(C)  | 30. | Ans.(D)  | 31. | Ans.(B)  | 32. | Ans(D)   |
| 33. | Ans(C)   | 34. | Ans (A)  | 35. | Ans.(C)  | 36. | Ans.(A)  |
| 37. | Ans.(B)  | 38. | Ans.(C)  | 39. | Ans.(A)  | 40. | Ans.(A)  |
| 41. | Ans.(C)  | 42. | Ans.(A)  | 43. | Ans.(A)  | 44. | Ans.(D)  |
| 45. | Ans.(B)  | 46. | Ans.(D)  | 47. | Ans.(B)  | 48. | Ans.(D)  |
| 49. | Ans. (B) | 50. | Ans.(D)  | 51. | Ans.(B)  | 52. | Ans.(C)  |
| 53. | Ans.(D)  | 54. | Ans.(A)  | 55. | Ans.(B)  | 56. | Ans.(C)  |
| 57. | Ans.(A)  | 58. | Ans.(C)  | 59. | Ans.(A)  | 60. | Ans(B)   |
| 61. | Ans (A)  | 62. | Ans. (A) | 63. | Ans.(A)  | 64. | Ans.(D)  |
| 65. | Ans.(C)  |     |          |     |          |     |          |

## EXERCISE O-II

|            |                                         |            |                                       |            |                   |            |                      |
|------------|-----------------------------------------|------------|---------------------------------------|------------|-------------------|------------|----------------------|
| <b>1.</b>  | <b>Ans.(B,D)</b>                        | <b>2.</b>  | <b>(A,B)</b>                          | <b>3.</b>  | <b>Ans.(A,D)</b>  | <b>4.</b>  | <b>Ans. (C)</b>      |
| <b>5.</b>  | <b>Ans.(A,C)</b>                        | <b>6.</b>  | <b>Ans. (A,B,C,D)</b>                 | <b>7.</b>  | <b>Ans. (C,D)</b> | <b>8.</b>  | <b>Ans. (D)</b>      |
| <b>9.</b>  | <b>Ans. (A, B)</b>                      | <b>10.</b> | <b>Ans.(A,C)</b>                      | <b>11.</b> | <b>Ans.(C,D)</b>  | <b>12.</b> | <b>Ans.(A, B, D)</b> |
| <b>13.</b> | <b>Ans (A, C)</b>                       | <b>14.</b> | <b>Ans.(A,C,D)</b>                    |            |                   |            |                      |
| <b>15.</b> | <b>Ans.(B)</b>                          | <b>16</b>  | <b>Ans.(D)</b>                        | <b>17.</b> | <b>Ans.(A)</b>    | <b>18</b>  | <b>Ans.(B)</b>       |
| <b>19</b>  | <b>Ans.(C)</b>                          | <b>20</b>  | <b>Ans.(C)</b>                        | <b>21</b>  | <b>Ans. (B)</b>   | <b>22.</b> | <b>Ans. (B)</b>      |
| <b>23.</b> | <b>Ans.(A)</b>                          | <b>24.</b> | <b>Ans.(C)</b>                        |            |                   |            |                      |
| <b>25.</b> | <b>Ans.(A)</b>                          | <b>26.</b> | <b>Ans.(A) R, (B) S, (C) P, (D) Q</b> |            |                   |            |                      |
| <b>27.</b> | <b>(A)-S; (B)- R ; (C) - O; (D) – P</b> |            |                                       |            |                   |            |                      |

**JEE-MAINS**

- |              |              |             |             |
|--------------|--------------|-------------|-------------|
| 1. Ans (1)   | 2. Ans (4)   | 3. Ans(3)   | 4. Ans(3)   |
| 5. Ans(4)    | 6. Ans(3)    | 7. Ans.(3)  |             |
| 8. Ans.(3)   | 9. Ans.(1)   | 10. Ans.(1) | 11. Ans.(1) |
| 12. Ans (3)  | 13. Ans.(4)  | 14. Ans.(1) | 15. Ans.(4) |
| 16. Ans. (3) | 17. Ans. (4) | 18. Ans.(4) | 19. Ans.(4) |

**JEE-ADVANCED**

- |                                    |                                    |
|------------------------------------|------------------------------------|
| 1. Ans.0.492 atmp ; 0.246 atmp     | 2. Ans.(C)                         |
| 3. Ans.123                         | 4. $-173^{\circ}\text{C}$ , 0.82 L |
| 5. Ans.XeF <sub>6</sub>            | 6. Ans.(C)                         |
| 7. Ans.Both statements are correct | 8. Ans.(D)                         |
| 9. Ans.(C)                         | 10. Ans.434.17 m/sec               |
| 11. Ans.(B)                        | 12. Ans.(4)                        |
| 13. Ans.(7)                        | 14. Ans.(C)                        |
| 15. Ans.(D)                        | 16. Ans.(2.22)                     |

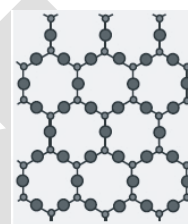
## SOLID STATE

## 1. THE SOLID STATE :

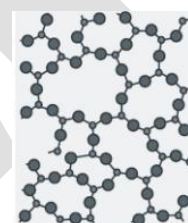
The solid are characterised by incompressibility, rigidity and mechanical strength. The molecules, atoms or ions in solids are closely packed i.e. they are held together by strong forces and can not move about at random. Thus solids have definite volume, shape, slow diffusion, low vapour pressure and possesses the unique property of being rigid.

## 2. AMORPHOUS AND CRYSTALLINE SOLIDS

Solids can be classified as *crystalline* or *amorphous* on the basis of the nature of order present in the arrangement of their constituent particles. A crystalline solid usually consists of a large number of small crystals, each of them having a definite characteristic geometrical shape. In a crystal, the arrangement of constituent particles (atoms, molecules or ions) is ordered. It has **long range order** which means that there is a regular pattern of arrangement of particles which repeats itself periodically over the entire crystal. Sodium chloride and quartz are typical examples of crystalline solids. An amorphous solid (Greek *amorphos* = no form) consists of particles of irregular shape. The arrangement of constituent particles (atoms, molecules or ions) in such a solid has only **short range order**. In such an arrangement, a regular and periodically repeating pattern is observed over short distances only.



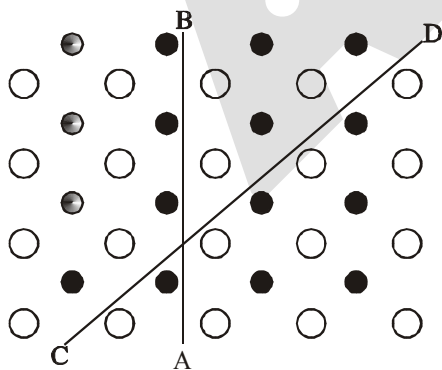
(a)



(b)

**Fig. 1.1 :** Two dimensional structure of (a) quartz and (b) quartz glass

Such portions are scattered and in between, the arrangement is disordered. The structures of quartz (crystalline) and quartz glass (amorphous) are shown in Fig. 1.1 (a) and (b) respectively. While the two structures are almost identical, yet in the case of amorphous quartz glass there is no *long range order*. The structure of amorphous solids is similar to that of liquids. Glass, rubber and plastics are typical examples of amorphous solids. Due to the differences in the arrangement of the constituent particles, the two types of solids differ in their properties.



**Fig. 1.2 :** Anisotropy in crystals is due to different arrangement of particles along different directions.

Crystalline solids have a sharp melting point. On the other hand, amorphous solids soften over a range of temperature and can be moulded and blown into various shapes. On heating they may become crystalline at some temperature. Some glass objects from ancient civilisations are found to become milky in appearance because of some crystallisation. Like liquids, amorphous solids have a tendency to flow, though very slowly. Therefore, sometimes these are called ***pseudo solids*** or ***super cooled liquids***. Glass panes fixed to windows or doors of old buildings are invariably found to be slightly thicker at the bottom than at the top. This is because the glass flows down very slowly and makes the bottom portion slightly thicker.

Crystalline solids are **anisotropic** in nature, that is, some of their physical properties like electrical resistance or refractive index show different values when measured along different directions in the same crystals. This arises from different arrangement of particles in different directions. This is illustrated in Fig. 1.2. Since the arrangement of particles is different along different directions, the value of same physical property is found to be different along each direction. Amorphous solids on the other hand are **isotropic** in nature. It is because there is no *long range* order in them and arrangement is irregular along all the directions. Therefore, value of any physical property would be same along any direction. These differences are summarised in Table below :

**Distinction between Crystalline and Amorphous Solids**

| Property                                      | Crystalline Solids                                                                                                 | Amorphous Solids                                                                   |
|-----------------------------------------------|--------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------|
| Shape                                         | Definite characteristic geometrical shape                                                                          | Irregular shape                                                                    |
| Melting point                                 | Melt at a sharp and characteristic temperature                                                                     | Gradually soften over a range of temperature                                       |
| Cleavage property                             | When cut with a sharp edged tool, they split into two pieces and the newly generated surfaces are plane and smooth | When cut with a sharp edged tool, they cut into two pieces with irregular surfaces |
| Heat of fusion                                | They have a definite and characteristic heat of fusion                                                             | They do not have definite heat of fusion                                           |
| Anisotropy                                    | Anisotropic in nature                                                                                              | Isotropic in nature                                                                |
| Nature                                        | True solids                                                                                                        | Pseudo solids or super cooled liquids                                              |
| Order in arrangement of constituent particles | Long range order                                                                                                   | Only short range order.                                                            |

**Ex.1** Classify the following as amorphous or crystalline solids :

- |                        |                 |
|------------------------|-----------------|
| (a) Polyurethane       | (b) Napthalene  |
| (c) Benzoic acid       | (d) Teflon      |
| (e) Potassium nitrate  | (f) Cellophane  |
| (g) Polyvinyl chloride | (h) Fibre glass |
| (i) Copper             |                 |

**Sol.** Crystalline : (b) , (c) , (e) , (i)

Amorphous : (a) , (d) , (f) , (g) , (h)

**Note :** Polymeric substances are generally amorphous.

## 3. TYPES OF THE CRYSTALLINE SOLID

| Types of Solid                 | Constituent Particles                           | Bonding/ Attractive forces  | Examples                                                                 | Physical Nature                | Electrical Conductivity                                                          | Melting Point |
|--------------------------------|-------------------------------------------------|-----------------------------|--------------------------------------------------------------------------|--------------------------------|----------------------------------------------------------------------------------|---------------|
| (1) Molecular Solids           | Molecules                                       |                             |                                                                          |                                |                                                                                  |               |
| (i) Non polar                  |                                                 | Dispersion or London forces | Ar, CCl <sub>4</sub> , H <sub>2</sub> , I <sub>2</sub> , CO <sub>2</sub> | Soft                           | Insulator                                                                        | Very low      |
| (ii) Polar                     |                                                 | Dipole-dipole               | HCl, SO <sub>2</sub>                                                     | Soft                           | Insulator                                                                        | Low           |
| (iii) Hydrogen bonded          |                                                 | Hydrogen bonding            | H <sub>2</sub> O (ice)                                                   | Hard                           | Insulator                                                                        | Low           |
| (2) Ionic Solids               | Ions                                            | Coulombic or electrostatic  | NaCl, MgO, ZnS, CaF <sub>2</sub>                                         | Hard but brittle               | Insulator in solid state but conductors in molten state and in aqueous solutions | High          |
| (3) Metallic Solids            | Positive ions in a sea of delocalised electrons | Metallic bonding            | Fe, Cu, Ag, Mg                                                           | Hard but malleable and ductile | Conductors in solid state as well as in molten state                             | Fairly high   |
| (4) Covalent or network Solids | Atoms                                           | Covalent bonding            | SiO <sub>2</sub> (quartz), SiC, C (diamond), AlN,                        | Hard                           | Insulators                                                                       | Very high     |
|                                |                                                 |                             | C(graphite)                                                              | Soft                           | Conductor                                                                        |               |

**Ex.2** Classify the following solids in different categories based on the nature of intermolecular forces operating in them :

- |                                                          |                                               |
|----------------------------------------------------------|-----------------------------------------------|
| (a) Potassium sulphate (K <sub>2</sub> SO <sub>4</sub> ) | (b) Tin (Sn)                                  |
| (c) Benzene (C <sub>6</sub> H <sub>6</sub> )             | (d) Urea (NH <sub>2</sub> CONH <sub>2</sub> ) |
| (e) Ammonia (NH <sub>3</sub> )                           | (f) Water (H <sub>2</sub> O)                  |
| (g) Zinc sulphide (ZnS)                                  | (h) Graphite (C)                              |
| (i) Rubidium (Rb)                                        | (j) Argon (Ar)                                |
| (k) Silicon carbide (SiC)                                | (l) Bronze                                    |

**Sol.** Ionic solids : (a), (g)

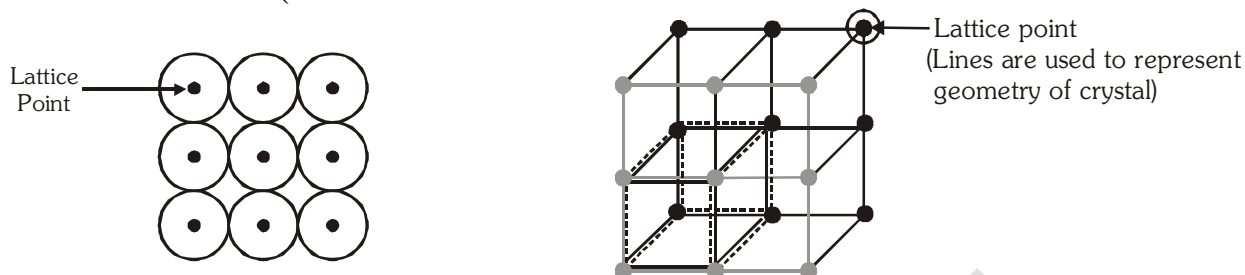
Metallic solids : (b), (i), (l)

Molecular solids : (c), (d), (e), (f), (j)

Covalent network solids.: (h), (k)

## 4.0 SOME BASIC DEFINITION :

### 4.1 SPACE LATTICE (CRYSTAL LATTICE :



The main characteristic of crystalline solids is a regular and repeating pattern of constituent particles. If the three dimensional arrangement of constituent particles in a crystal is represented diagrammatically, in which each particle is depicted as a point, the arrangement is called crystal lattice. Thus, **a regular three dimensional arrangement of points in space is called a crystal lattice**. A portion of a crystal lattice is shown in Fig. The following are the characteristics of a crystal lattice:

- Each point in a lattice is called **lattice point** or **lattice site**.
- Each point in a crystal lattice represents one constituent particle which may be an atom, a molecule (group of atoms) or an ion.
- Lattice points are joined by straight lines to bring out the geometry of the lattice.

### 4.2. UNIT CELL :

Unit cell is the smallest portion of a crystal lattice which, when repeated in different directions, generates the entire lattice.

A unit cell is characterized by the edge lengths  $a$ ,  $b$  and  $c$  along the three edges of the unit cell and the angles  $\alpha$ ,  $\beta$  and  $\gamma$  between the pair of edges :  $bc$ ,  $ca$  and  $ab$ , respectively.

#### TYPE OF UNIT CELLS -

#### 4.2.1 Primitive and Centred Unit cells

Unit cells can be broadly divided into two categories, primitive and centred unit cells.

##### (a) Primitive Unit Cells (P)

When constituent particles are present only on the corner positions of a unit cell, it is called as **primitive unit cell**.

##### (b) Centred Unit Cells

When a unit cell contains one or more constituent particles present at positions other than corners in addition to those at corners, it is called a centred unit cell. **Centred unit cells** are of three types:

- Body-Centred Unit Cells (I) :** Such a unit cell contains one constituent particle (atom, molecule or ion) at its body-centre besides the ones that are at its corners.
- Face-Centred Unit Cells (F) :** Such a unit cell contains one constituent particle present at the centre of each face, besides the ones that are at its corners.
- End-Centred Unit Cells (E) :** In such a unit cell, one constituent particle is present at the centre of any two opposite faces besides the ones present at its corners.



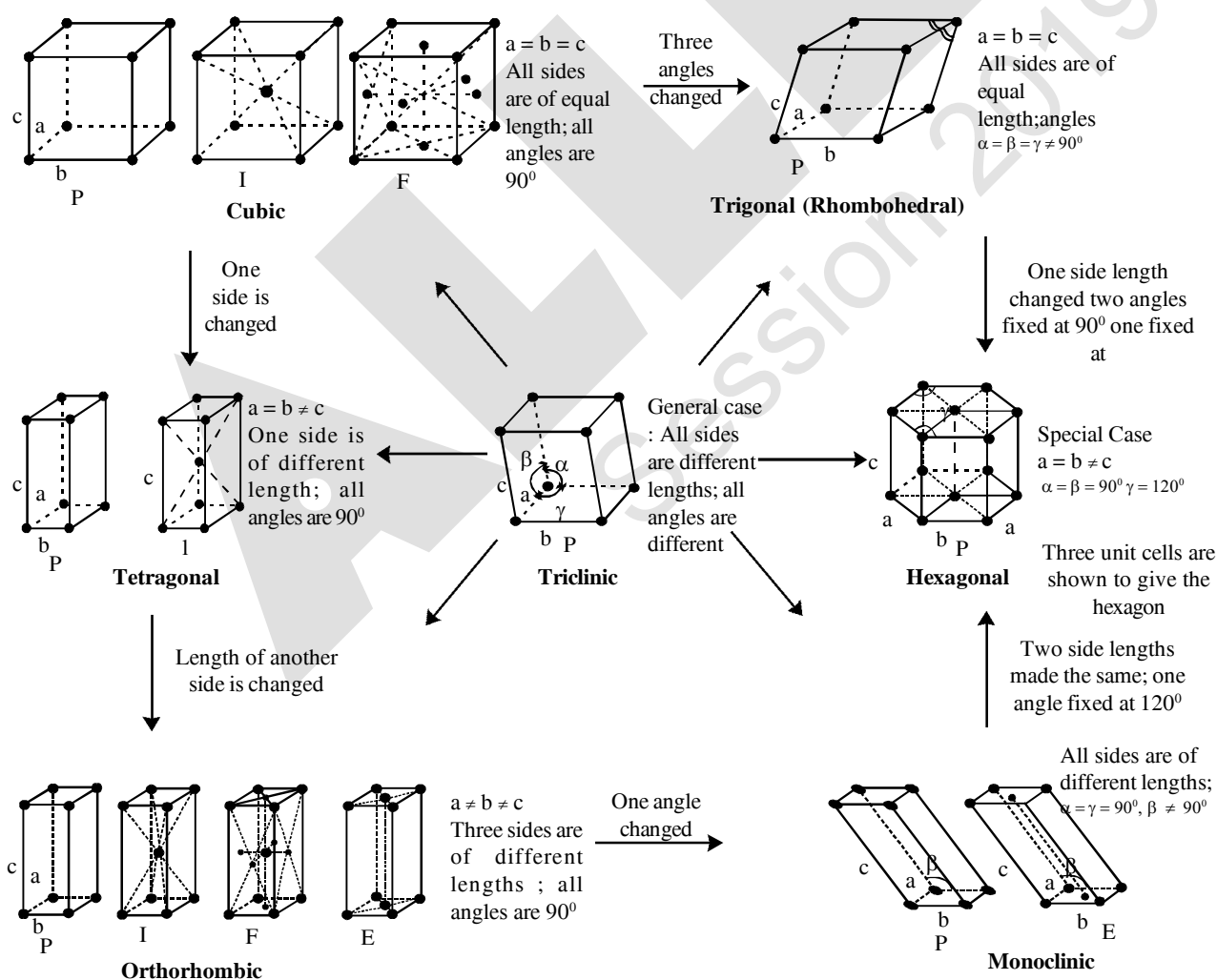
## 4.3. THE SEVEN CRYSTAL SYSTEMS

On the basis of the classification of symmetry, the lattice have been divided into seven systems. These can be grouped into 7 crystal systems. These seven systems with the characteristics of their axes (angles and intercepts) along with some examples of each are given in the following table :

Seven Primitive Unit cells and their Possible Variations as Centred Unit Cells

| Crystal system           | Possible Variations                                | Axial distance or edge lengths | Axial angles                                      | Examples                                                                                                |
|--------------------------|----------------------------------------------------|--------------------------------|---------------------------------------------------|---------------------------------------------------------------------------------------------------------|
| Cubic                    | Primitive, body-centred, Face centre               | $a = b = c$                    | $\alpha = \beta = \gamma = 90^\circ$              | NaCl, Zinc blende, Cu                                                                                   |
| Tetragonal               | Primitive, Body-centred                            | $a = b \neq c$                 | $\alpha = \beta = \gamma = 90^\circ$              | White tin, $\text{SnO}_2$ , $\text{TiO}_2$ , $\text{CaSO}_4$                                            |
| Orthorhombic             | Primitive, Body-centred, Face-centred, End-centred | $a \neq b \neq c$              | $\alpha = \beta = \gamma = 90^\circ$              | Rhombic sulphur, $\text{KNO}_3$ , $\text{BaSO}_4$                                                       |
| Hexagonal                | Primitive                                          | $a = b \neq c$                 | $\alpha = \beta = 90^\circ, \gamma = 120^\circ$   | Graphite, ZnO, CdS,                                                                                     |
| Rhombohedral or Trigonal | Primitive                                          | $a = b = c$                    | $\alpha = \beta = \gamma \neq 90^\circ$           | Calcite ( $\text{CaCO}_3$ ), HgS (Cinnabar)                                                             |
| Monoclinic               | Primitive, End-centred                             | $a \neq b \neq c$              | $\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$ | Monoclinic sulphur, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$                                 |
| Triclinic                | Primitive                                          | $a \neq b \neq c$              | $\alpha \neq \beta \neq \gamma \neq 90^\circ$     | $\text{K}_2\text{Cr}_2\text{O}_7$ , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , $\text{H}_3\text{BO}_3$ |

## 4.4. BRAVAIS LATTICES : There are 14 Bravais lattices :



#### 4.5. CO-ORDINATION NUMBER :

The number of nearest particles around a specific particle in a given crystalline substance is called *co-ordination* number.

#### 4.6. PACKING EFFICIENCY OR PACKING DENSITY (P.E.) :

Packing efficiency is defined as the ratio of volume occupied by the constituent particles to the total volume of the crystalline substance.

$$\text{P.E.} = \frac{\text{Volume occupied by particles present in a crystal}}{\text{Volume of crystal}}$$

$$\text{P.E.} = \frac{\text{Volume occupied by particles present in unit cell}}{\text{Volume of Unit Cell}}$$

$$\text{P.E.} = \frac{Z \times (4/3)\pi r^3}{V}, \text{ where } Z = \text{number of atoms present in unit cell}$$

#### 4.7. DENSITY OF THE CRYSTAL :

$$\text{Density of crystal} = \text{Density of an unit cell} = \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}}$$

$$\text{Mass of the unit cell} = \text{Number of particles present in a unit cell} \times \text{Mass of one particles} = Z \times m$$

$$\text{But mass of one particles (m)} = \frac{\text{Particle mass}}{\text{Avogadro Number}} = \frac{M}{N_A}$$

$$\text{Mass of an unit cell} = Z \times \frac{M}{N_A}$$

$$\text{Density of an unit cell} = \frac{Z \times \frac{M}{N_A}}{V}$$

$$\therefore \text{Density of Crystal, } d = \text{Density of an unit cell} = \frac{Z \times M}{V \times N_A} \text{ g cm}^{-3}$$

#### 5.0 ANALYSIS OF CUBIC CRYSTAL :

##### 5.1. GEOMETRY OF A CUBE

Number of corners = 8

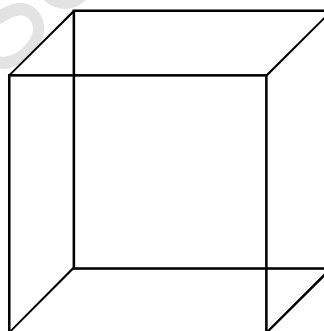
Number of faces = 6

Number of edges = 12

Number of cube centre = 1

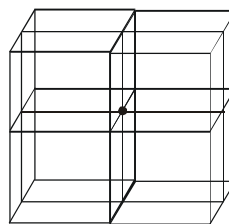
Number of cube diagonals = 4

Number of face diagonals = 12

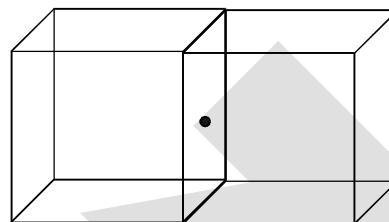


**5.2 CONTRIBUTION OF A CONSTITUENT PARTICLE AT DIFFERENT SITES OF CUBE :****5.2.1** A corner of a cube is common in 8 cubes.

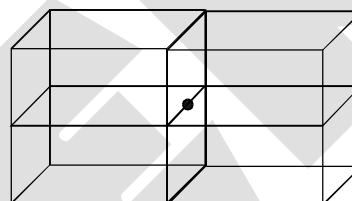
So  $\frac{1}{8}$  th part of a particle is present at this corner of cube.

**5.2.2** A face of a cube is common in 2 cubes.

So  $\frac{1}{2}$  th part of a particle is present at the face of a cube.

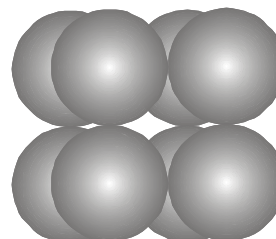
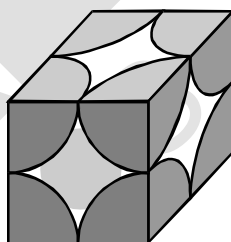
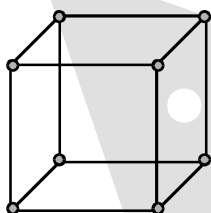
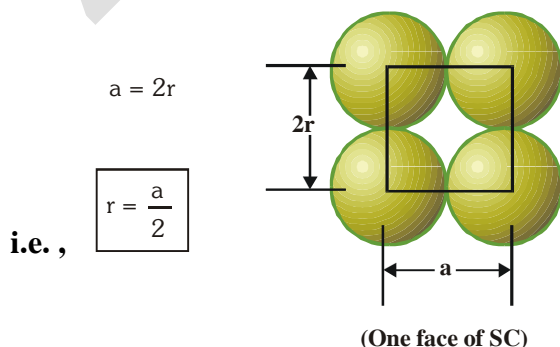
**5.2.3** An edge of a cube is common in four cubes,

so  $\frac{1}{4}$  th part of particle is present at the edge of a cube

**5.3 TYPE OF CUBIC UNIT CELL :****5.3.1 Simple/Primitive/Basic Unit cell (Simple cubic, SC) ;**

A unit cell having lattice point only at corners called as primitive or simple unit cell. In this case there is one particle at each of the eight corners of the unit cell.

Considering a particles at one corner as the centre, it will be found that this atom is surrounded by six equidistant neighbours (particles) and thus the co-ordination number will be six. If 'a' is the side of the unit cell, then the distance between the nearest neighbours shall be equal to 'a'.

**(a) Relationship between Edge length 'a' and Particle radius 'r' :-**

(b) **Number of particles present in unit cell (Z) :** In this case one particle lies at each corner. Hence simple cubic unit cell contains a total of  $\frac{1}{8} \times 8 = 1$  particle/unit cell.

(c) **Packing efficiency (P. E.) :**

$$\text{P.E.} = \frac{\text{Volume occupied by particles present in unit cell}}{\text{Volume of unit cell}} = \frac{Z \times \frac{4}{3} \pi r^3}{V} \quad \left[ \text{Volume of atom} = \frac{4}{3} \pi r^3 \right]$$

$$\text{P.E.} = \frac{1 \times \frac{4}{3} \times \pi \times \left(\frac{a}{2}\right)^3}{a^3} = \frac{\pi}{6} = 0.52 \quad \text{or} \quad 52\% \quad \left[ r = \frac{a}{2} \text{ and } V = a^3, Z = 1 \right]$$

In SC, 52% of total volume is occupied by particles.

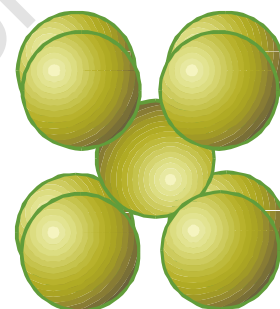
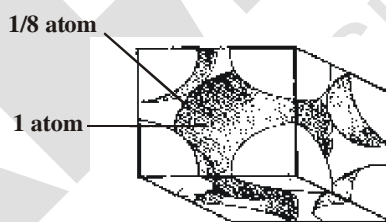
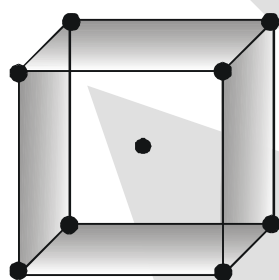
$\therefore$  Void space  $\approx (100 - 52) = 48\%$

(d) **Coordination number (CN)**

| Nearest neighbour | Distance    | Number |
|-------------------|-------------|--------|
| 1                 | a           | 6      |
| 2                 | $\sqrt{2}a$ | 12     |
| 3                 | $\sqrt{3}a$ | 8      |

### 5.3.2. Body Centred Cubic unit cell (BCC):

A unit cell having lattice point at the body centre in addition to the lattice points at every corner is called as body centered unit cell. Here the central particle is surrounded by eight equidistant particles and hence the co-ordination number is eight. The nearest distance between two particles will be  $\frac{a\sqrt{3}}{2}$

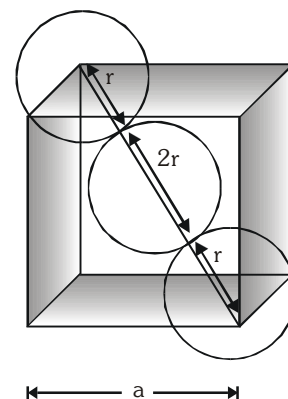


(a) **Relationship between edge length 'a' and particle radius 'r' :**

In BCC, along cube diagonal all particles touches each other and the length of cube diagonal is  $\sqrt{3}a$ .

$$\text{So,} \quad \sqrt{3}a = 4r$$

$$\text{i.e.} \quad r = \frac{\sqrt{3}a}{4}$$



(b) Number of particle present in unit cell (Z):

$$Z = \left( \frac{1}{8} \times 8 \right) + (1 \times 1) = 1 + 1 = 2 \text{ particles/unit cell.}$$

(Corner)

(Body centre)

In this case one particle lies at the each corner of the cube. Thus contribution of the 8 corners is  $\left( \frac{1}{8} \times 8 \right) = 1$ , while that of the body centred is 1 in the unit cell. Hence total number of particles per unit cell is  $1 + 1 = 2$

(c) Packing efficiency :

$$\text{P.E.} = \frac{Z \times \frac{4}{3} \pi r^3}{V} = \frac{2 \times \frac{4}{3} \times \pi \left( \frac{\sqrt{3}a}{4} \right)^3}{a^3} = \frac{\sqrt{3}\pi}{8} = 0.68 \text{ or } 68\% \quad [Z = 2, r = \frac{\sqrt{3}a}{4}, V = a^3]$$

In BCC, 68% of total volume is occupied by particles.

$$\therefore \text{Void space} = 100 - 68 = 32\%$$

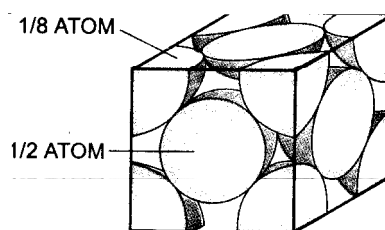
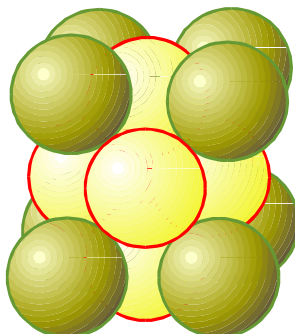
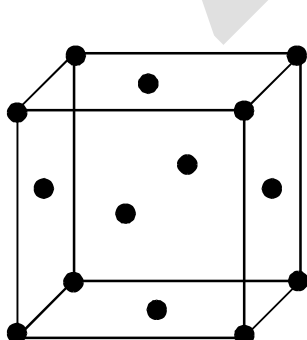
(d) Coordination number (CN)

| Nearest neighbour | Distance               | Number |
|-------------------|------------------------|--------|
| 1                 | $\sqrt{3} \frac{a}{2}$ | 8      |
| 2                 | a                      | 6      |
| 3                 | $\sqrt{2} a$           | 12     |

### 5.3.3 Face Centred Cubic unit cell (FCC):

A unit cell having lattice point at every face centre in addition to the lattice point at every corner called as face centred unit cell.

In this case there are eight particles at the eight corners of the unit cell and six particles at the centre of six faces. Considering a particle at the face centre as origin, it will be found that this face is common to two cubes and there are twelve points surrounding it situated at a distance which is equal to half the face diagonal of the unit cell. Thus the co-ordination number will be twelve and the distance between the two nearest particles will be  $\frac{a}{\sqrt{2}}$ .

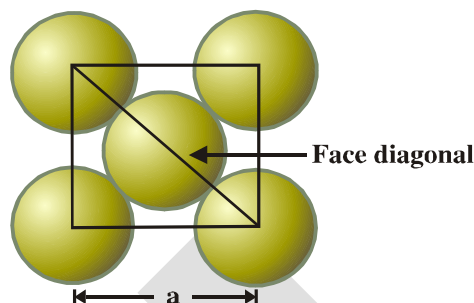


(a) Relationship between edge length 'a' and atomic radius 'r' :

In FCC, along the face diagonal all atoms touches each other and the length of face diagonal is  $\sqrt{2}a$ .

$$\text{So } 4r = \sqrt{2}a$$

$$\text{i.e. } r = \frac{a}{2\sqrt{2}}$$



(b) Number of particles per unit cell : (Z)

$$Z = \left(\frac{1}{8} \times 8\right) + \left(6 \times \frac{1}{2}\right) = 1 + 3 = 4 \text{ particles/unit cell}$$

Corner faces

In this case, one particle lies at the each corner of the cube and one particle lies at the centre of each face of the cube. It may noted that only 1/2 of each face sphere lie within the unit cell and there are six such faces. The total contribution of 8 corners is  $\left(\frac{1}{8} \times 8\right) = 1$ , while that of 6 face centred particles is  $\left(\frac{1}{2} \times 6\right) = 3$  in the unit cell.

Hence, total number of particles per unit cell is  $1 + 3 = 4$

(c) Packing efficiency :

$$\text{P.E.} = \frac{Z \times \frac{4}{3} \pi r^3}{V} \quad [Z = 4, r = \frac{a}{2\sqrt{2}}, V = a^3]$$

$$= \frac{4 \times \frac{4}{3} \pi \times \left(\frac{a}{2\sqrt{2}}\right)^3}{a^3} = \frac{\pi}{3\sqrt{2}} = 0.74 \text{ or } 74\%$$

In FCC, 74% of total volume is occupied by particles. This is maximum for crystals having identical particles.

$$\therefore \text{Void space} = 100 - 74 = 26 \%$$

(d) Coordination number (CN)

| Nearest neighbour | Distance               | Number |
|-------------------|------------------------|--------|
| 1                 | $\frac{a}{\sqrt{2}}$   | 12     |
| 2                 | a                      | 6      |
| 3                 | $\sqrt{\frac{3}{2}} a$ | 24     |

## 5.4 SUMMARY OF CUBIC CRYSTAL :

| Unit cell              | No. of particles per unit cell (Z) | 2r =                  | CN | Volume occupied by particles (%) |
|------------------------|------------------------------------|-----------------------|----|----------------------------------|
| Simple cube(SC)        | 1                                  | a                     | 6  | 52                               |
| Body centred cube(BCC) | 2                                  | $\frac{a\sqrt{3}}{2}$ | 8  | 68                               |
| Face centred cube(FCC) | 4                                  | $\frac{a}{\sqrt{2}}$  | 12 | 74                               |

**Ex.3.** An element (atomic mass = 60) having face centred cubic crystal has a density of  $6.23 \text{ g cm}^{-3}$ . What is the edge length of the unit cell ? (Avogadro constant,  $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$ )

**Sol.** Since element has fcc structure hence there are 4 atoms in a unit cell ( $Z = 4$ ), Atomic mass is 60 ( $M = 60$ ),  $N_A = 6.02 \times 10^{23}$  and  $d = 6.23 \text{ g cm}^{-3}$ .

$$\therefore d = \frac{Z \times M}{V \times N_A}$$

$$\text{or } V = \frac{Z \times M}{d \times N_A} = \frac{(4)(60 \text{ g mol}^{-1})}{(6.23 \text{ g cm}^{-3})(6.02 \times 10^{23} \text{ mol}^{-1})} = 64 \times 10^{-24} \text{ cm}^3$$

Let  $\ell$  be the length of the edge of the unit cell.

$$\therefore \ell^3 = V = 64 \times 10^{-24} \text{ cm}^3 \quad \text{or} \quad \ell = 4.0 \times 10^{-8} \text{ cm}$$

**Ex.4.** The density of Al is  $5.4 \text{ g/cm}^3$ . If it crystallise in fcc lattice, determine its atomic radius.

$$\text{Sol. } d = \frac{ZM}{N_A \cdot V} \Rightarrow 5.4 = \frac{4 \times 27}{N_A \times (2\sqrt{2}r)^3}$$

$$\therefore r = 1.136 \times 10^{-8} \text{ cm} = 1.136 \text{ \AA}$$

**Ex.5.** A solid crystallises in cubic crystal in which 'X' atoms occupy all the corners and body centres and 'Y' atoms occupy all the face-centres. What is the simplest formula of solid?

$$\text{Sol. } Z_X = 8 \times \frac{1}{8} + 1 = 2$$

$$Z_Y = 6 \times \frac{1}{2} = 3$$

$$\therefore \text{Simplest formula of solid} = X_2Y_3$$

## 6. CLOSE PACKING OF IDENTICAL SOLID SPHERES

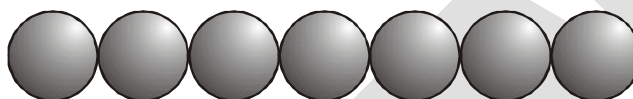
The solids which have non-directional bonding, their structures are determined on the basis of geometrical consideration. For such solids, it is found that the lowest energy structure is that in which each particle is surrounded by the greatest possible number of neighbours. In order to understand the structure of such solids, let us consider the particles as hard sphere of equal size in three directions. Although there are many ways to arrange the hard spheres but the one in which maximum available space is occupied will be economical which is known as **closed packing**.

To clearly understand the packing of these spheres, the packing can be categorised as :

- (i) Close packing in one dimension.
- (ii) Close packing in two dimension.
- (iii) Close packing in three dimension.

### 6.1 CLOSE PACKING IN ONE DIMENSION :

In one dimension , only one arrangement of spheres is possible as shown in fig.



Close packing of spheres in one dimension

Each sphere is touched by other two spheres, hence coordination numbers of packing is two.

### 6.2 CLOSE PACKING IN TWO DIMENSION :

Two possible types of two dimensional packing are

- (i) Square close packing in two dimension.
- (ii) Hexagonal close packing in two dimension.

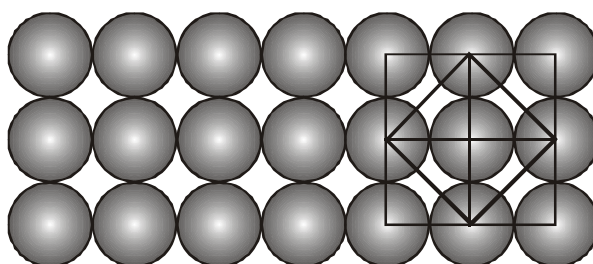
#### (i) Square close packing in two dimension :

When two rows are placed in such a manner, that spheres of one row are placed immediately below of the other, the resulting packing is called two dimensional square close packing.

- (i) Since all the rows are identical, the packing is called AAA ..... type packing.
- (ii) Each sphere is touched by four other, hence coordination number is four.
- (iii) If centres of spheres are connected, square cells are formed , hence it also called two dimensional square packing.
- (iv) This type of packing is not very effective in terms of utilisation of space.

$$(v) \text{ Packing efficiency in 2-D} = \frac{1 \times \pi r^2}{a^2} = \frac{1 \times \pi (a/2)^2}{a^2} = \frac{\pi}{4} = 0.78 \text{ or } 78\%$$

$$(vi) \text{ Packing efficiency in 3-D} = \frac{1 \times \frac{4}{3} \pi \left(\frac{a}{2}\right)^3}{a^3} = 0.52 \text{ or } 52\% \text{ [In 3-D, its unit cell is simple cubic]}$$





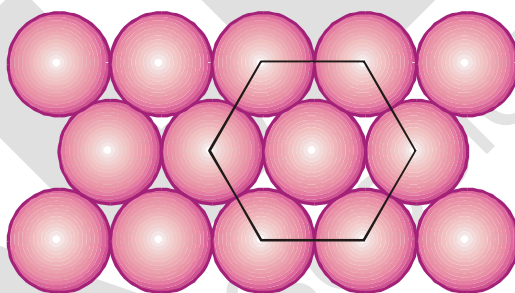
**(ii) Hexagonal close packing in two dimension :**

If various one dimensional close pack rows are placed in such a way that spheres of top row fits in depression of bottom row spheres, the resulting packing is called two dimensional hexagonal close packing.

- (i) Every third row sphere comes exactly at top of first row sphere, hence the packing is called ABABAB ..... packing.
- (ii) If centres are joined, hexagonal unit cells are formed. Hence this is called two dimensional hexagonal close packing.
- (iii) This packing is most efficient in utilising space in two dimensional arrangement.
- (iv) Each sphere is touched by six other, hence coordination number is six.

$$(v) \text{ Packing efficiency in 2-D} = \frac{3 \times \pi \left(\frac{a}{2}\right)^2}{\frac{a^2 \sqrt{3}}{4} \times 6} = \frac{\pi}{2\sqrt{3}} = 0.90 \text{ or } 90\%$$

$$(vi) \text{ Packing efficiency in 3-D} = \frac{3 \times \frac{4}{3} \pi \left(\frac{a}{2}\right)^3}{\frac{a^2 \sqrt{3}}{4} \times 6 \times a} = \frac{\pi}{3\sqrt{3}} = 0.60 \text{ or } 60\%$$

**6.3 CLOSE PACKING IN THREE DIMENSIONS :**

When two dimensional packing structure are arranged one above the other, depending upon type of two dimensional arrangement in a layer, and the relative positions of spheres in above or below layer, various types of three dimensional packing results. To define 3-D lattice, six lattice parameters are required - 3 edge lengths & 3 angles.

- (i) Simple cubic packing (A A A A .....)
- (ii) Hexagonal close packing (AB AB AB .....)
- (iii) Cubic close packing or face centred cubic (ABC ABC...)

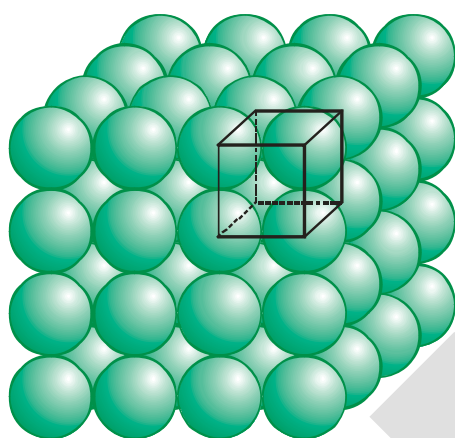
### 6.3.1 Three dimensional close packing from square two dimensional packing

#### (Simple cubic packing in three dimension)

The two dimensional square close packed layer are placed, in such a manner that spheres in each layer comes immediately on top of below layer, simple cubic packing results. Important points :

- (i) Spheres all aligned vertically and horizontally in all directions.
- (ii) The unit cell for this packing is simple cubic unit cell.
- (iii) In this packing, only 52% of available space is occupied by spheres.
- (iv) Each sphere is in contact with six spheres and hence coordination number is 6.

$$(v) \text{ Packing efficiency} = \frac{1 \times \frac{4}{3} \pi r^3}{(2r)^3} = \frac{\pi}{6} \approx 0.52$$



Simple cubic lattice formed by  
A A A ... arrangement

Coordination number = 6

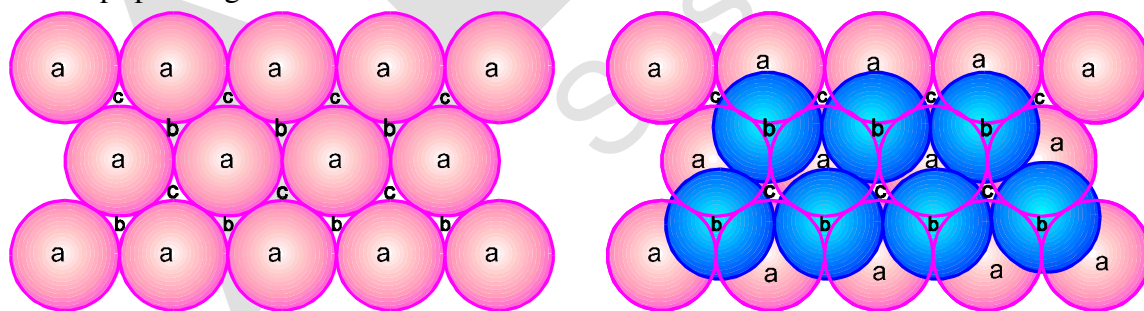
First neighbour = 6 at a distance =  $a$

Second neighbour = 12 at  $(\sqrt{2}a)$  distance

Third neighbour = 8 at  $(\sqrt{3}a)$  distance

### 6.3.2 Three dimensional close packing from hexagonal two dimensional packing :

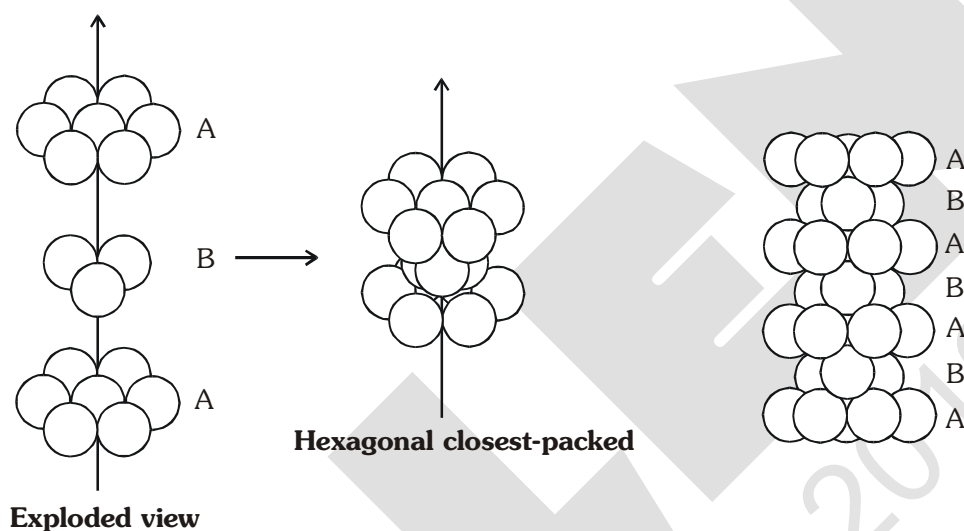
In hexagonal close packing, there are two types of the voids (open space or space left) which are divided into two sets 'b' and 'c' for convenience. The spaces marked 'c' are curved triangular spaces with tips pointing upwards whereas spaces marked 'b' are curved triangular spaces with tips pointing downwards.



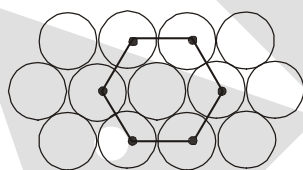
Now we extend the arrangement of spheres in three dimensions by placing second close packed layer (hexagonal close packing) (B) on the first layer (A). The spheres of second layer may be placed either on space denoted by 'b' or 'c'. It may be noted that it is not possible to place spheres on both types of voids (i.e. b and c). Thus half of the voids remain unoccupied by the second layer. The second layer also have voids of the types 'b' and in order to build up the third layer, there are following ways :

**(I) Hexagonal close packing (HCP)**

- (i) In one way, the spheres of the third layer lie on the spaces of second layer (B) in such a way that they lie directly above those in the first layer (A). In other words we can say that the third layer becomes identical to the first layer. Such arrangement is called AB AB AB ....type packing or hexagonal close packing (hcp).
- (ii) Maximum possible space is occupied by spheres.
- (iii) Each sphere is touched by 12 other spheres in 3D (6 in one layer, 3 in top layer and 3 in bottom) and hence the coordination number is 12.

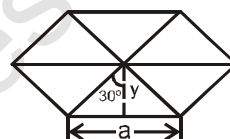
**(iv) Packing efficiency of HCP units****Relation between a, b, c and R :**

$$a = b = 2R$$



$$\tan 30^\circ = \frac{a}{2 \times y}$$

So



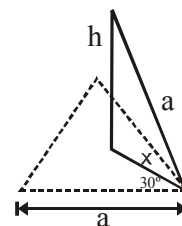
$$y = \frac{a \times \sqrt{3}}{2 \times 1} = \frac{\sqrt{3}}{2} a$$

$$\text{Base Area} = 6 \left[ \frac{1}{2} \times \frac{a}{2} \times \frac{\sqrt{3}}{2} a \right] = \frac{6\sqrt{3}a^2}{4}$$

**Calculation of c :**

$$\cos 30^\circ = \frac{a}{2 \times x}$$

$$x = \frac{2a}{2 \times \sqrt{3}} = \frac{a}{\sqrt{3}}$$



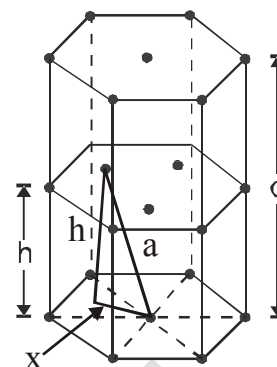
Applying pythagoras theorem :  $x^2 + h^2 = a^2$

$$\text{So } h^2 = a^2 - x^2 = a^2 - \frac{a^2}{3} = \frac{2}{3} a^2$$

$$h = \sqrt{\frac{2}{3}} a \quad \text{so} \quad c = 2h = 2\sqrt{\frac{2}{3}} a$$

So volume of hexagon = area of base  $\times$  height

$$= \frac{6\sqrt{3}}{4} \times a^2 \times 2\sqrt{\frac{2}{3}} a = \frac{6\sqrt{3}}{4} \times (2R)^2 + 2\sqrt{\frac{2}{3}} \times (2R) = 24\sqrt{2} R^3$$



(v) **Effective no. of particles (Z)**

$$Z = 3 + 2 \times \frac{1}{2} + 12 \times \frac{1}{6} = 3 + 1 + 2 = 6.$$

It must be noted that all three spheres of 'B' layer are not exactly inside the unit cell. But the contribution of three spheres are taken because the same volume of other spheres in that layer is also inside the unit cell.

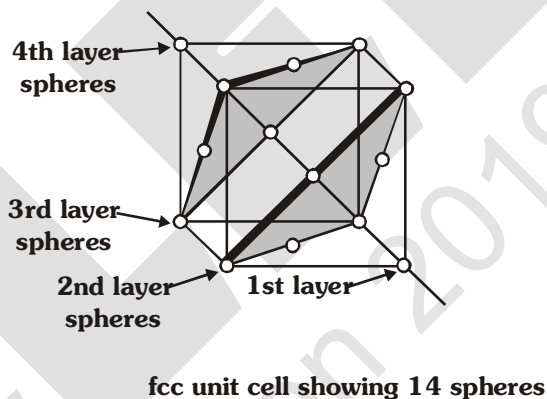
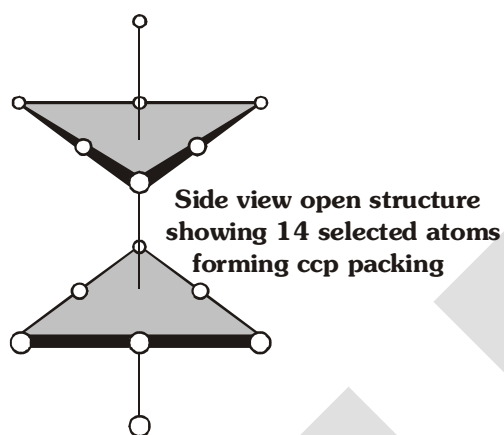
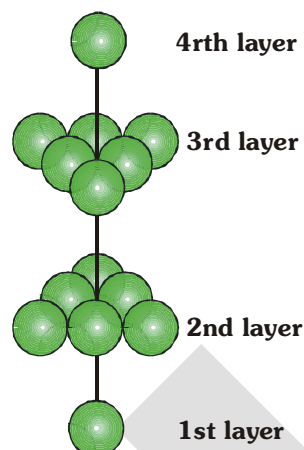
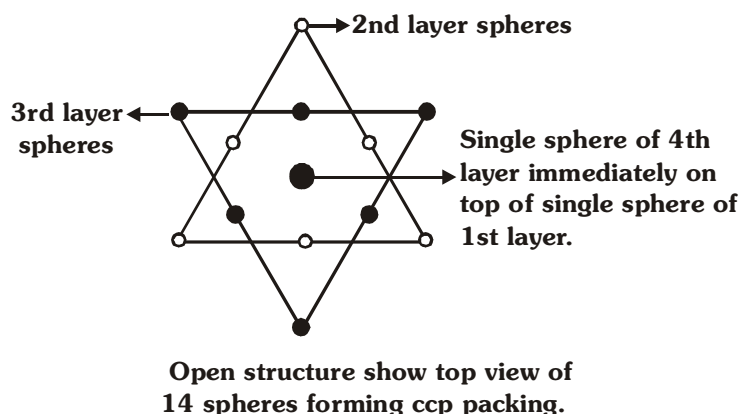
(vi) **Packing efficiency**  $= \frac{6 \times \frac{4}{3} \pi R^3}{24\sqrt{2} R^3} = \frac{\pi}{3\sqrt{2}} = 0.74 \text{ or } 74\%.$

(vii) **Density (d)**  $= \frac{\text{mass}}{\text{volume}} = \left[ \frac{Z \times M}{N_A \times \text{volume}} \right]$

(II) **Cubic close packing (CCP) or face centered cubic (FCC)**

In second way, the spheres of the third layer (C) lie on the second layer (B) in such a way that they lie over the unoccupied spaces 'C' of the first layer (A). If this arrangement is continued in the same order every fourth layer becomes identical to the first. Such arrangement of particle is called ABC ABC ABC.... or cubic close packing (ccp) or face centered cubic (fcc).

It may be noted that in ccp (or fcc) structures, each sphere is surrounded by 12 spheres hence the coordination number of each sphere is 12. The spheres occupy 74% of the total volume and 26% of is the empty space in both (hcp and ccp) structures.



(i) Relation between 'a' and 'R' :

$$a \neq 2R$$

$$\sqrt{2}a = 4R \quad (\text{sphere are touching along the face diagonal})$$

(ii) Effective no. of particles per unit cell (Z)

$$Z = \frac{1}{8} \times 8 + \frac{1}{2} \times 6 = 4$$

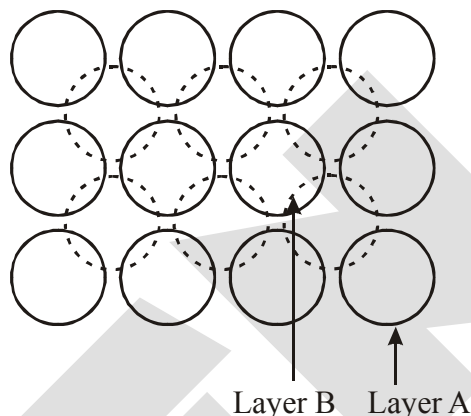
(iii) Packing fraction :

$$\text{P.F.} = \frac{4 \times \frac{4}{3} \pi R^3}{4 \times 4 \times 4 R^3} \times \sqrt{2} \times 2 = \frac{\pi}{3\sqrt{2}} = 0.74 \text{ or } 74\%$$

(iv) Density (d) =  $\frac{Z \times M}{N_A \times a^3}$

### 6.3.3

There is another possible arrangement of packing of spheres known as body centred cubic (bcc) arrangement. This arrangement is observed in square close packing in which there is suitable space between the spheres in each layer. In bcc arrangement, the spheres of the second layer lie at the space (hollows or voids) in the first layer.



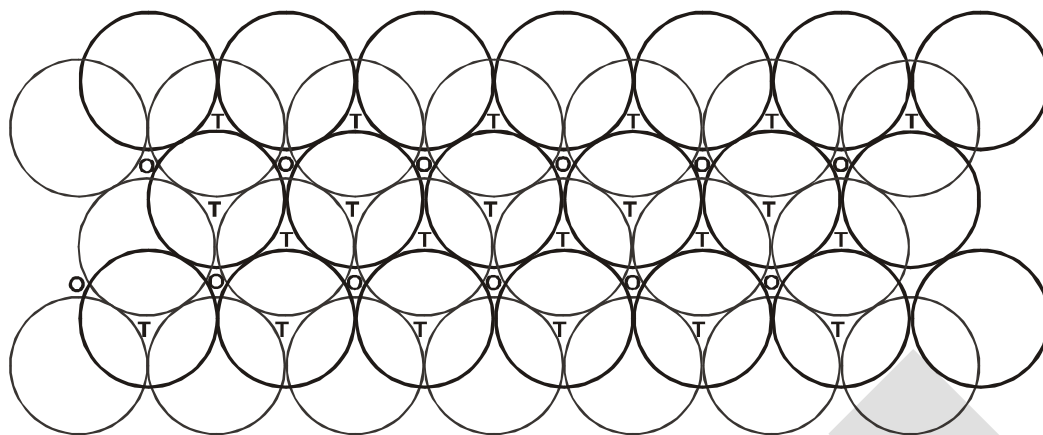
Thus each sphere of the second layer touches four spheres of the first layer. Now spheres of the third layer are placed exactly about the spheres of first layer. In this way each sphere of the second layer touches eight spheres (four of 1st layer and four of IIIrd layer). Therefore coordination number of each sphere is 8 in bcc sturcture. The spheres occupy 68% of the total volume 32% of the volume is the empty space.

## 7. STRUCTURES OF VARIOUS ELEMENTS

[illegible]

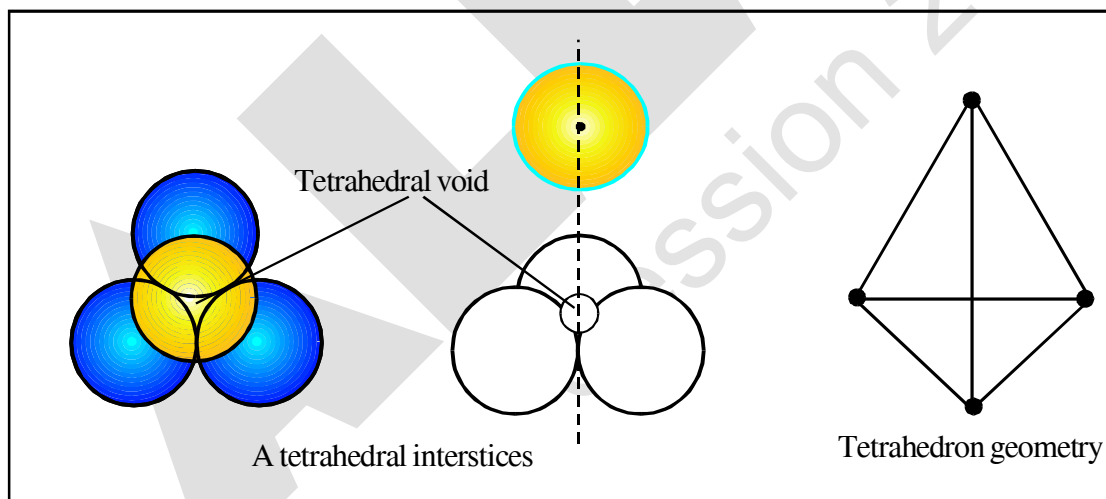
## 8. INTERSTICES OR VOIDS OR HOLES IN CRYSTALS

It has been shown that the particles are closely packed in the crystals even though there is some empty space left in between the spheres. This is known as interstices (or interstitial site or hole or empty space or voids). In three dimensional close packing (CCP & HCP) the interstices are of two types : (i) tetrahedral voids and (ii) octahedral voids.



A stack of two layers of close packed spheres and voids generated in them. T = Tetrahedral void; O = Octahedral void

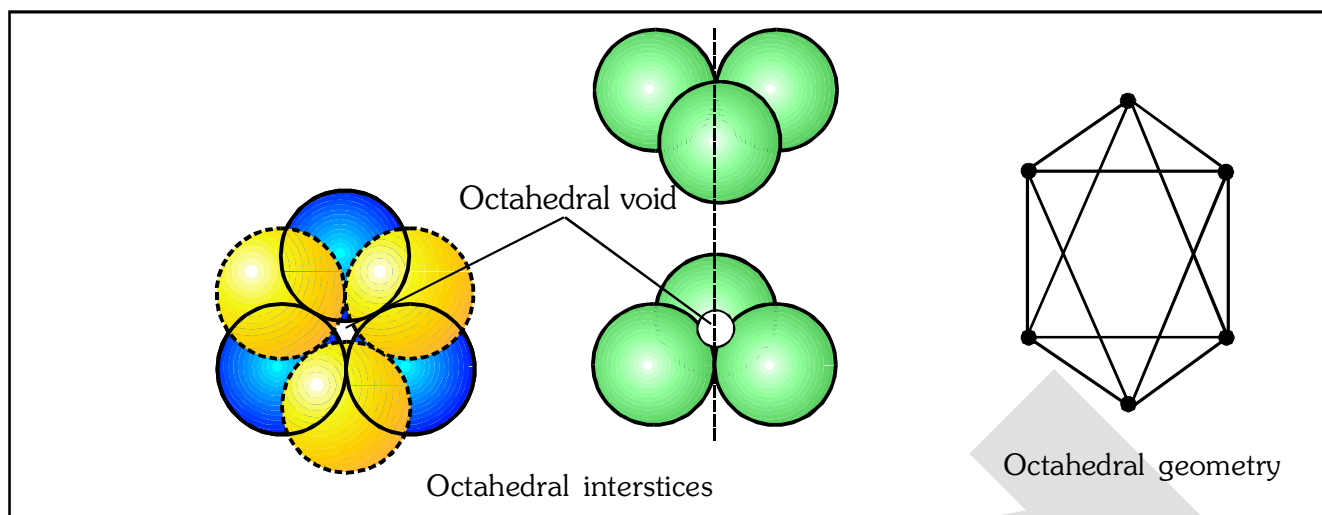
- (i) **Tetrahedral voids :** We have seen that in hexagonal close packing (hcp) and cubic close packing (ccp), each sphere of second layer touches with three spheres of first layer. Thus, they leave a small space in between which is known as **tetrahedral site or interstices**. In another words, the vacant space between 4 touching spheres is called as tetrahedral void. Since a sphere touches three spheres in the below layer and three spheres in the above layer hence there are two tetrahedral sites associated with one sphere. It may be noted that a tetrahedral site does not mean that the site is tetrahedral in geometry but it means that this site is surrounded by four spheres and the centres of these four spheres lie at the apices of a regular tetrahedron.



- (ii) **Octahedral voids :** Hexagonal close packing (hcp) and cubic close packing (ccp) also form another type of interstices (or site), which is called octahedral site (or interstices). In another words, the vacant space between 6 touching spheres is called as octahedral void.

In the figure two layers of close packed spheres are shown. The spheres of first layer are shown by full circles while that of second layer by dotted circles. Two triangles are drawn by joining the centres of three touching spheres of both the layers.

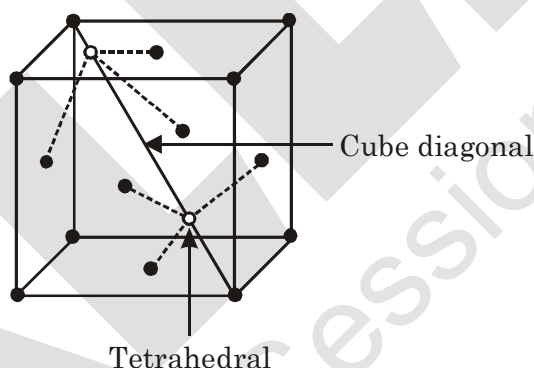




The apices of these triangles point are in opposite directions. On super imposing these triangles on one another, an octahedral site is created. It may be noted that an octahedral site does not mean that the hole is octahedral in shape but it means that this site is surrounded by six nearest neighbour lattice points arranged octahedrally.

### 8.1 POSITIONS OF TETRAHEDRAL VOIDS IN AN FCC UNIT CELL :

In FCC, one corner and its three face centred atom of faces meeting at that corner form a tetrahedral void. In FCC, two tetrahedral voids are obtained along one cube diagonal. So in FCC 8 tetrahedral voids are present.



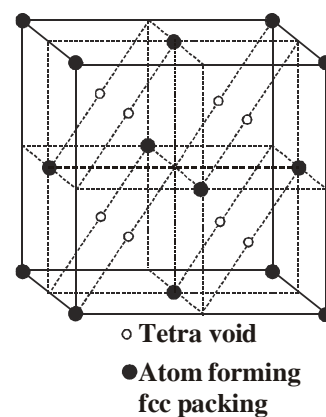
Alternatively, the centre of tetrahedral void is located on the centre

of body diagonal of each small cube of volume  $\left(\frac{a^3}{8}\right)$ .

$$\text{Total number of particles per unit cell} = \frac{1}{2} \times 6 + 8 \times \frac{1}{8} = 4$$

Total number of tetrahedral void = 8

$\therefore$  Effective number of tetrahedral void per particle = 2.







### 9. CRYSTAL OF DIAMOND

The crystal is FCC for C atom & alternate tetrahedral voids are also occupied by carbon atoms.

$$* Z = \frac{1}{8} \times 8 + 6 \times \frac{1}{2} + 4 = 8$$

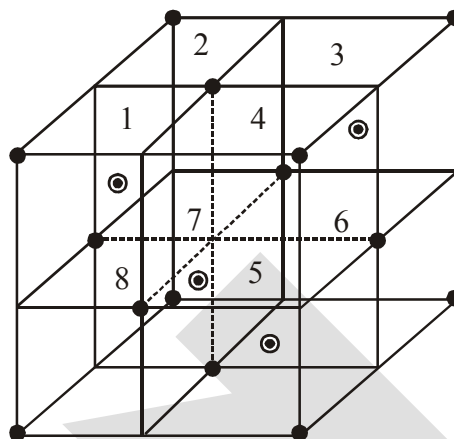
$$* CN = 4$$

$$* \frac{\sqrt{3}a}{4} = 2r = d_{C-C}$$

$$* \text{Number of C-C bonds/unit cell} = 4 \times 4 = 16$$

$$* \text{Number of C-C bonds/C-atom} = \frac{16}{8} = 2$$

$$* PE = \frac{8 \times \frac{4}{3} \pi r^2}{\left(\frac{8r}{\sqrt{3}}\right)^3} = \frac{\sqrt{3}\pi}{16} \approx 0.34 \text{ or } 34\%$$



### CLASS ILLUSTRATION

**Ex.6** A solid crystallises in close packing for 'P' atoms and 25% of tetrahedral voids are occupied by 'Q' atoms. What is the simplest formula of solid ?

**Sol.**  $Z_P = 1$  (say)

$$Z_Q = \frac{25}{100} \times 2 = \frac{1}{2}$$

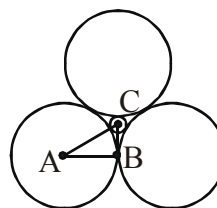
$$\therefore \text{Simplest formula of solid} = PQ_{1/2} = P_2Q$$

**Ex.7** Calculate the radius (r) of largest sphere which may be fitted in the (i) triangular voids (ii) tetrahedral voids (iii) octahedral voids (iv) cubic voids made by identical spheres of radius, 'R', without disturbing the crystal.

**Sol.** (i)  $AB = R$   
 $AC = R + r$   
 $\angle BAC = 30^\circ$

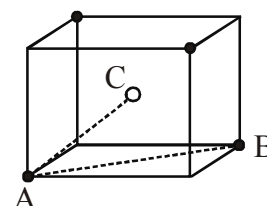
$$\text{Now, } \cos 30^\circ = \frac{AB}{AC} \Rightarrow \frac{\sqrt{3}}{2} = \frac{R}{R+r}$$

$$r = \left( \frac{2}{\sqrt{3}} - 1 \right) R = 0.155R$$



(ii)  $AB = \sqrt{2}a = 2R$

$$AC = \frac{\sqrt{3}a}{2} = R + r$$



$$\text{Now, } \frac{R+r}{R} = \frac{\sqrt{3}}{\sqrt{2}}$$

$$\therefore r = \left( \sqrt{\frac{3}{2}} - 1 \right) R = 0.225R$$

$$\text{(iii) } AB = R$$

$$AC = R + r$$

$$\angle BAC = 45^\circ$$

$$\text{Now, } \cos 45^\circ = \frac{AB}{AC} \Rightarrow \frac{1}{\sqrt{2}} = \frac{R}{R+r}$$

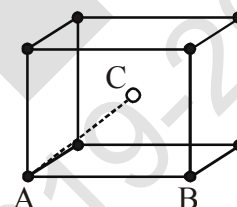
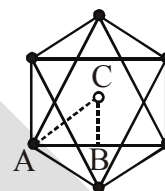
$$\therefore r = (\sqrt{2} - 1)R = 0.414R$$

$$\text{(iv) } AB = a = 2R$$

$$AC = \frac{\sqrt{3}a}{2} = R + r$$

$$\text{Now, } \frac{R+r}{R} = \sqrt{3}$$

$$\therefore r = (\sqrt{3} - 1)R = 0.732R$$



**Ex.8** An element (molar mass = 60 gm/mole) crystallises in CCP lattice. If density is 6.25 gm/cm<sup>3</sup> and the distance between next nearest neighbour is  $d\text{\AA}$ , then the value of 'd' is ( $N_A = 6 \times 10^{23}$ ).

**Ans. (4)**

$$d = \frac{ZM}{N_A \cdot a^3}$$

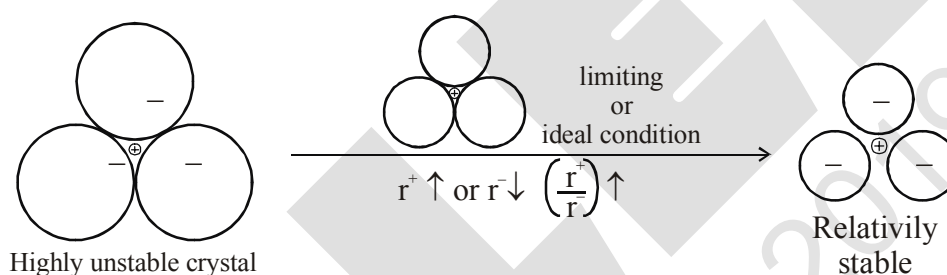
$$6.25 = \frac{4 \times 60}{6 \times 10^{23} \times a^3} \Rightarrow a = 4 \times 10^{-8} \text{ cm} = 4\text{\AA}.$$

## 10 PACKING IN IONIC SOLID

- (i) Normally anions are bigger than cations, hence ionic solid are considered as the packing of anions and cations are supposed to occupy the voids.
- (ii) Oppositely charged particles should lie closer and similarly charged particles should lie away from each other.
- (iii) Each ion tend to maximise its coordination number (Number of oppositely charged ions around it).

Point (ii) and (iii) contradict each other because on increase the CN, the repulsion between like charges will also increases. Hence, in all the ionic solids, there must be a balance with the help of relative size of ions to ensure maximum CN and minimum repulsion between like charges.

### 10.1 LIMITING OR IDEAL RADIUS RATION $\left(\frac{r^+}{r^-}\right)$ :



The minimum  $\frac{r^+}{r^-}$  values for the existence of a cation in a particular void is called **limiting radius ratio** for that void.

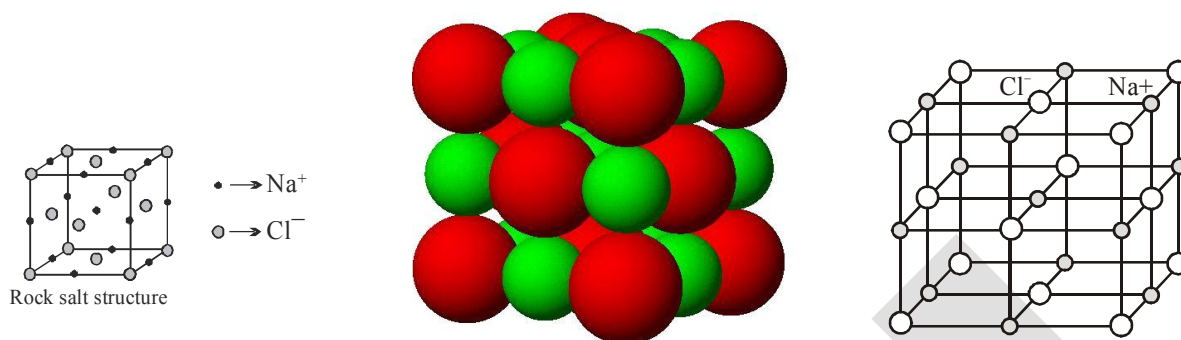
With the increase in radius ratio, space between anion will increase & hence the cation may tend for higher coordination number.

| Voids       | CN | Limiting $r^+/r^-$ | Range of $r^+/r^-$ |
|-------------|----|--------------------|--------------------|
| Triangular  | 3  | 0.155              | 0.155 – 0.225      |
| Tetrahedral | 4  | 0.225              | 0.225 – 0.414      |
| Octahedral  | 6  | 0.414              | 0.414 – 0.732      |
| Cubic       | 8  | 0.732              | 0.732 – 1.000      |

\* For values lesser than 0.155, crystal will not exist.

## 10.2 TYPES OF IONIC STRUCTURES:

## 10.2.1 Rock salt structure (NaCl):



The bigger  $\text{Cl}^-$  forms cubic close packing and small  $\text{Na}^+$  occupy positions of all octahedral voids. The radius ratio  $\frac{r^+}{r^-}$  lie in the range 0.414 – 0.732.

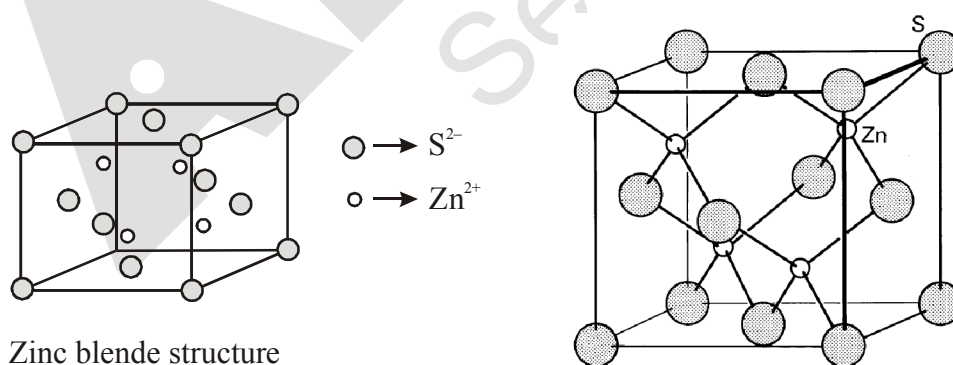
- (i) Each  $\text{Na}^+$  is surrounded by six  $\text{Cl}^-$  and each  $\text{Cl}^-$  is surrounded by six  $\text{Na}^+$  ion. [6:6 coordination]
- (ii) No. of  $\text{Na}^+$  and  $\text{Cl}^-$  in each unit cell is 4.
- (iii) Number of formula units of NaCl per unit cell is equal to 4.

(iv) The density of NaCl crystal is given by  $d = \left( \frac{4 \times M_{\text{NaCl}}}{N_A \times a^3} \right)$

(v) The edge length of NaCl unit cell is given by  $(2r^+ + 2r^-) \Rightarrow \frac{a}{2} = r^+ + r^-$

10.2.2 Zinc blende (sphalerite) structure ( $\text{ZnS}$ ):

Larger ion ( $\text{S}^{2-}$ ) forming ccp arrangement and smaller ion ( $\text{Zn}^{2+}$ ) filling half or alternate tetrahedral voids



- (i) C.N. of  $\text{Zn}^{2+} = 4$  ; C.N. of  $\text{S}^{2-} = 4$  [4 : 4 coordination]

(ii) Formula units of ZnS per unit cell = 4. (iii)  $d_{\text{ZnS}} = \frac{4 \times M_{\text{ZnS}}}{N_A \times a^3}$  (iv)  $r_{\text{Zn}^{2+}} + r_{\text{S}^{2-}} = \frac{a\sqrt{3}}{4}$

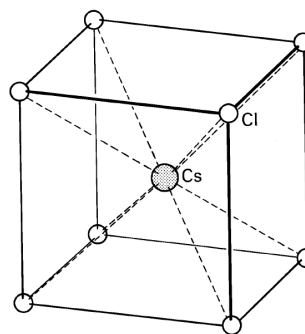
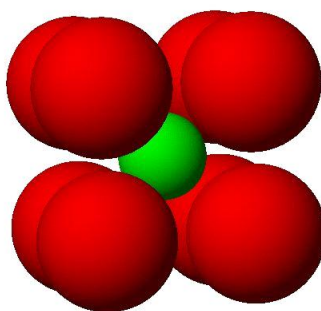
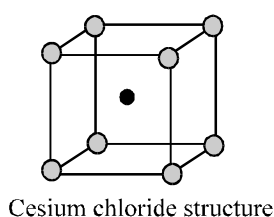
### 10.2.3 Cesium chloride structure (CsCl) :

$\text{Cl}^-$  at the corners of cube and  $\text{Cs}^+$  in the center (cubic void).

- (i) C.N. of  $\text{Cs}^+ = 8$  ; C.N. of  $\text{Cl}^- = 8$  [8 : 8 coordination]  
 (ii) Formula units of CsCl per unit cell = 1

(iii)  $d_{\text{CsCl}} = \frac{M_{\text{CsCl}}}{N_A \times a^3}$

(iv)  $r_{\text{Cs}^+} + r_{\text{Cl}^-} = \frac{a\sqrt{3}}{2} \Rightarrow \boxed{r^+ + r^- = \frac{a\sqrt{3}}{2}}$



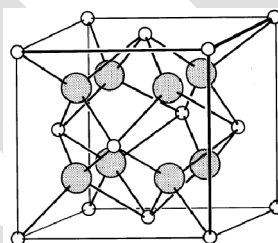
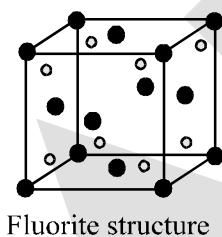
### 10.2.4 Fluorite structure ( $\text{CaF}_2$ ) :

$\text{Ca}^{2+}$  forming ccp arrangement and  $\text{F}^-$  filling all tetrahedral voids.

- (i) C.N. of  $\text{F}^- = 4$  ; C.N. of  $\text{Ca}^{2+} = 8$  [8 : 4 coordination]  
 (ii) Formula units of  $\text{CaF}_2$  per unit cell = 4

(iii)  $d_{\text{CaF}_2} = \frac{4 \times M_{\text{CaF}_2}}{N_A \times a^3}$

(iv)  $r_{\text{Ca}^{2+}} + r_{\text{F}^-} = \frac{a\sqrt{3}}{4}$



### 10.2.5 Antifluorite structure ( $\text{Li}_2\text{O}$ ) :

$\text{O}^{2-}$  ion forming ccp and  $\text{Li}^+$  taking all tetrahedral voids.

- (i) C.N. of  $\text{Li}^+ = 4$   
 C.N. of  $\text{O}^{2-} = 8$   
 (ii) Formula units of  $\text{Li}_2\text{O}$  ; per unit cell = 4

(iii)  $d_{\text{Li}_2\text{O}} = \frac{4 \times M_{\text{Li}_2\text{O}}}{N_A \times a^3}$

(iv)  $r_{\text{Li}^+} + r_{\text{O}^{2-}} = \frac{a\sqrt{3}}{4}$

### 10.2.6 Corundum Structure ( $\text{Al}_2\text{O}_3$ ) :

$\text{O}^{2-}$  forming hcp and  $\text{Al}^{3+}$  filling 2/3 octahedral voids.

**10.2.7 Rutile structure ( $\text{TiO}_2$ ) :**

$\text{O}^{2-}$  forming hcp while  $\text{Ti}^{4+}$  ions occupy half of the octahedral voids.

**10.2.8 Pervoskite structure ( $\text{CaTiO}_3$ ) :**

$\text{Ca}^{2+}$  in the corner of cube,  $\text{O}^{2-}$  at the face center and  $\text{Ti}^{4+}$  at the centre of cube.

**10.2.9 Spinel and inverse spinel structure ( $\text{MgAl}_2\text{O}_4$ ) :**

$\text{O}^{2-}$  forming fcc,  $\text{Mg}^{2+}$  filling 1/8 of tetrahedral voids and  $\text{Al}^{3+}$  taking half of octahedral voids.

In an inverse spinel structure,  $\text{O}^{2-}$  ion form FCC lattice,  $\text{A}^{2+}$  ions occupy 1/8 of the tetrahedral voids and trivalent cation occupies 1/8 of the tetrahedral voids and 1/4 of the octahedral voids.

**Ex.9** A solid  $\text{A}^+\text{B}^-$  has NaCl type close packed structure. If the anion has a radius of 250 pm, what should be the ideal radius for the cation ? Can a cation  $\text{C}^+$  having a radius of 180 pm be slipped into the tetrahedral site of the crystal  $\text{A}^+\text{B}^-$  ? Give reason for your answer.

**Sol.** In  $\text{Na}^+\text{Cl}^-$  crystal each  $\text{Na}^+$  ion is surrounded by 6  $\text{Cl}^-$  ions and vice versa. Thus  $\text{Na}^+$  ion is placed in octahedral hole.

The limiting radius ratio for octahedral site = 0.414

$$\text{or } \frac{A^+}{B^-} = \frac{r}{R} = 0.414$$

Given that radius of anion ( $B^-$ )  $R = 250$  pm

i.e. radius of cation ( $A^+$ )  $r = 0.414 R = 0.414 \times 250$  pm

$$\text{or } r = 103.5 \text{ pm}$$

Thus ideal radius for cation ( $A^+$ ) is  $r = 103.5$  pm.

We know that ( $r/R$ ) for tetrahedral hole is 0.225.

$$\therefore \frac{r}{R} = 0.225$$

$$\text{or } r = 0.225 R = 0.225 \times 250 = 56.25 \text{ pm}$$

Thus ideal radius for cation is 56.25 pm for tetrahedral hole. But the radius of  $\text{C}^+$  is 180 pm. It is much larger than ideal radius i.e. 56.25 pm. Therefore we can not slip cation  $\text{C}^+$  into the tetrahedral site.

**Ex.10** A compound forms hexagonal close-packed structure. What is the total number of voids in 0.5 mole of it? How many of these are tetrahedral voids?

**Sol.** Since, for every atom forming hcp structure there are two tetrahedral voids and one octahedral void.

$$\text{Total voids} = 3 \times 0.5 = 1.5 \text{ mol and total tetrahedral void} = 2 \times 0.5 = 1 \text{ mol.}$$

**Ex.11** A compound is formed by two elements M and N. The element N forms ccp and atoms of M occupy 1/3rd of tetrahedral voids. What is the formula of the compound?

**Sol.** In one unit cell of ccp, no. of N = 4 ; total no. of tetrahedral void = 8 ; occupied tetrahedral void by M = 8/3 ; Empirical formula :  $\text{N}_4\text{M}_{8/3} = \text{N}_3\text{M}_2$ .

## 11. IMPERFECTIONS IN SOLIDS

Although crystalline solids have short range as well as long range order in the arrangement of their constituent particles, yet crystals are not perfect. Usually a solid consists of an aggregate of large number of small crystals. These small crystals have defects in them. This happens when crystallisation process occurs at fast or moderate rate. Single crystals are formed when the process of crystallisation occurs at extremely slow rate. Even these crystals are not free of defects.

The defects are basically irregularities in the arrangement of constituent particles. Broadly speaking, the defects are of two types, namely, **point defects** and **line defects**. Point defects are the irregularities or deviations from ideal arrangement around a point or an atom in a crystalline substance, whereas the line defects are the irregularities or deviations from ideal arrangement in entire rows of lattice points. These irregularities are called crystal defects. We shall confine our discussion to point defects only.

### 11.1 Types of Point Defects

Point defect can be classified into three types:

- (i) Stoichiometric defects
- (ii) Non-stoichiometric defects
- (iii) Impurity added defect

#### (i) Stoichiometric Defect

These are the point defect that do not disturb the stoichiometry of the solid. They are also called **intrinsic** or **thermodynamic defects**. Basically these are of two types; vacancy defects and interstitial defect.

##### (a) Vacancy Defect :

When some of the lattice sites are vacant, the crystal is said to have vacancy defect. This results in decrease in density of the substance. This defect can also develop when a substance is heated.

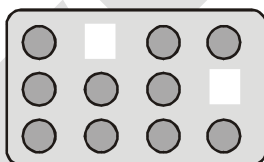


Fig. : Vacancy defects

**(b) Interstitial Defect :** When some constituent particles (atoms or molecules) occupy an interstitial site, the crystal is said to have interstitial defect. This defect increases the density of the substance.

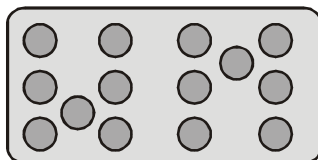


Fig. : Interstitial defects

Vacancy and interstitial defects as explained above can be shown by non-ionic solids. Ionic solids must always maintain electrical neutrality. Rather than simple vacancy or interstitial defects, they show these defects as **Frenkel** and **Schottky defects**.



(c) **Frenkel Defect** : This defect is shown by ionic solids.

The smaller ion (usually cation) is delocalised from its normal site to an interstitial site. It creates a vacancy defect at its original site and an interstitial defect at its new location.

Frenkel defect is also called **dislocation defect**. It does not change the density of the solid.

Frenkel defect is shown by ionic substance in which there is a large difference in the size of ions, for example, ZnS, AgCl, AgBr and AgI due to small size of  $\text{Zn}^{2+}$  and  $\text{Ag}^+$  ions.

**Influences** : Makes solid crystals good conductor. In Frenkel defect, ions in interstitial sites increase the dielectric constant.

(d) **Schottky Defect** : It is basically a vacancy defect in ionic solids. In order to maintain electrical neutrality, the number of missing cations and anions are equal (in stoichiometric ratio)

Like simple vacancy defect, Schottky defect also decreases the density of the substance. Number of such defects in ionic solids is quite significant. For example, in NaCl there are approximately,

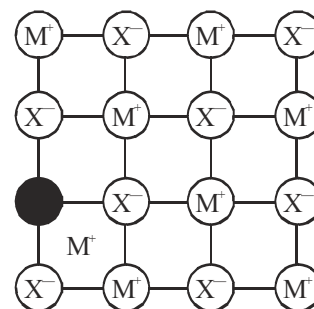
$10^6$  Schottky pairs per  $\text{cm}^3$  at room temperature. In  $1 \text{ cm}^3$  there are about  $10^{22}$  ions. Thus, there is one Schottky defect per  $10^{16}$  ions. Schottky defect is shown by ionic substances in which the cation and anion are of almost similar sizes. For example, NaCl, KCl, CsCl and AgBr. It may be noted that AgBr shows both, Frenkel as well as Schottky defects.

**Influence** : The presence of large number of schottky defects in crystal results in significant decrease in its density.

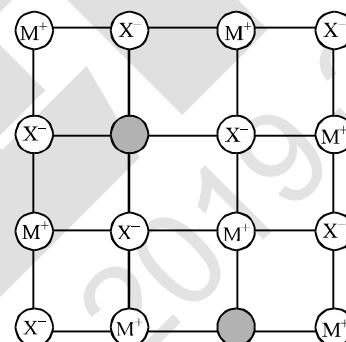
## (ii) Non-Stoichiometric Defects

The defects discussed so far do not disturb the stoichiometry of the crystalline substance. However, a large number of non-stoichiometric inorganic solids are known which contain the constituent elements in non-stoichiometric ratio due to defects in their crystal structures. These defects are of two types:

- Metal excess defect.
- Metal deficiency defect.



Frenkel Defect



Schottky Defect

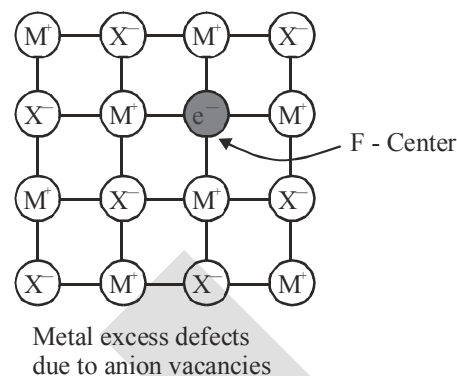
(a) Metal Excess Defect

(I) Metal excess defect due to anionic vacancies :

Alkali halides like NaCl and KCl show this type of defect. When crystals of NaCl are heated in an atmosphere of sodium vapour, the sodium atoms are deposited on the surface of the crystal. The  $\text{Cl}^-$  ions diffuse to the surface of the crystal and combine with Na atoms to give NaCl. This happens by loss of electron by sodium atoms to form  $\text{Na}^+$  ions.

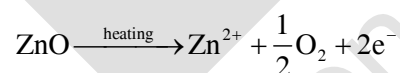
The released electrons diffuse into the crystal and occupy anionic sites. As a result the crystal now has an excess of sodium. The anionic sites occupied by unpaired electrons are called **F-centres** (from the German word *Farbenzenter* for colour centre).

They impart yellow colour to the crystals of NaCl. The colour results by excitation of these electrons when they absorb energy from the visible light falling on the crystals. Similarly, excess of lithium makes LiCl crystals pink and excess of potassium makes KCl crystals violet (or lilac).

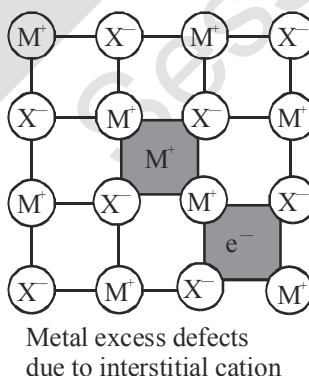


(II) Metal excess defect due to the presence of extra cations at interstitial sites :

Zinc oxide is white in colour at room temperature. On heating it loses oxygen and turns yellow.



Now there is excess of zinc in the crystal and its formula becomes  $\text{Zn}_{1+x}\text{O}$ . The excess  $\text{Zn}^{2+}$  ions move to interstitial sites and the electrons to neighbouring interstitial sites.

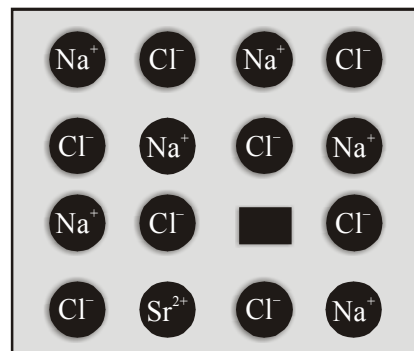


(b) Metal Deficiency Defect

There are many solids which are difficult to prepare in the stoichiometric composition and contain less amount of the metal as compared to the stoichiometric proportion. A typical example of this type is FeO which is mostly found with a composition of  $\text{Fe}_{0.95}\text{O}$ . It may actually range from  $\text{FeO}_{0.93}$  to  $\text{Fe}_{0.96}\text{O}$ . In crystals of FeO, some  $\text{Fe}^{2+}$  cations are missing and the loss of positive charge is made up by the presence of required number of  $\text{Fe}^{3+}$  ions.

**(iii) Impurity Defects**

If molten NaCl containing a little amount of  $\text{SrCl}_2$  is crystallised, some of the sites of  $\text{Na}^+$  ions are occupied by  $\text{Sr}^{2+}$ . Each  $\text{Sr}^{2+}$  replaces two  $\text{Na}^+$  Ions. It occupies the site of one ion and the other site remains vacant. The cationic vacancies thus produced are equal in number to that of  $\text{Sr}^{2+}$  ions. Another similar example is the solid solution of  $\text{CdCl}_2$  and  $\text{AgCl}$ .



Introduction of cation vacancy in NaCl by substitution of  $\text{Na}^+$  by  $\text{Sr}^{2+}$

- Note:** (i) As temperature increases, no. of defects increases exponentially.
- (ii) For defect formation :  $\Delta H > 0$ ,  $\Delta S > 0$   
 $\therefore$  More spontaneous at higher temperatures.
- (iii) No matter how many imperfections are present in a crystal, it is always electrically neutral (no net charge).

**12. ELECTRICAL PROPERTIES**

Solids exhibit an amazing range of electrical conductivities, extending over 27 orders of magnitude ranging from  $10^{-20}$  to  $10^7 \text{ ohm}^{-1} \text{ m}^{-1}$ . Solids can be classified into three types on the basis of their conductivities.

- (i) **Conductors** : The solids with conductivities ranging between  $10^4$  to  $10^7 \text{ ohm}^{-1} \text{ m}^{-1}$  are called conductors. Metals having conductivities in the order of  $10^7 \text{ ohm}^{-1} \text{ m}^{-1}$  are good conductors.
- (ii) **Insulators** : These are the solids with very low conductivities ranging between  $10^{-20}$  to  $10^{-10} \text{ ohm}^{-1} \text{ m}^{-1}$ .
- (iii) **Semiconductors** : These are the solids with conductivities in the intermediate range from  $10^{-6}$  to  $10^4 \text{ Ohm}^{-1} \text{ m}^{-1}$ .

**12.1 : Conduction of Electricity in Metals**

A conductor may conduct electricity through movement of electrons or ions. Metallic conductors belong to the former category and electrolytes to the latter.

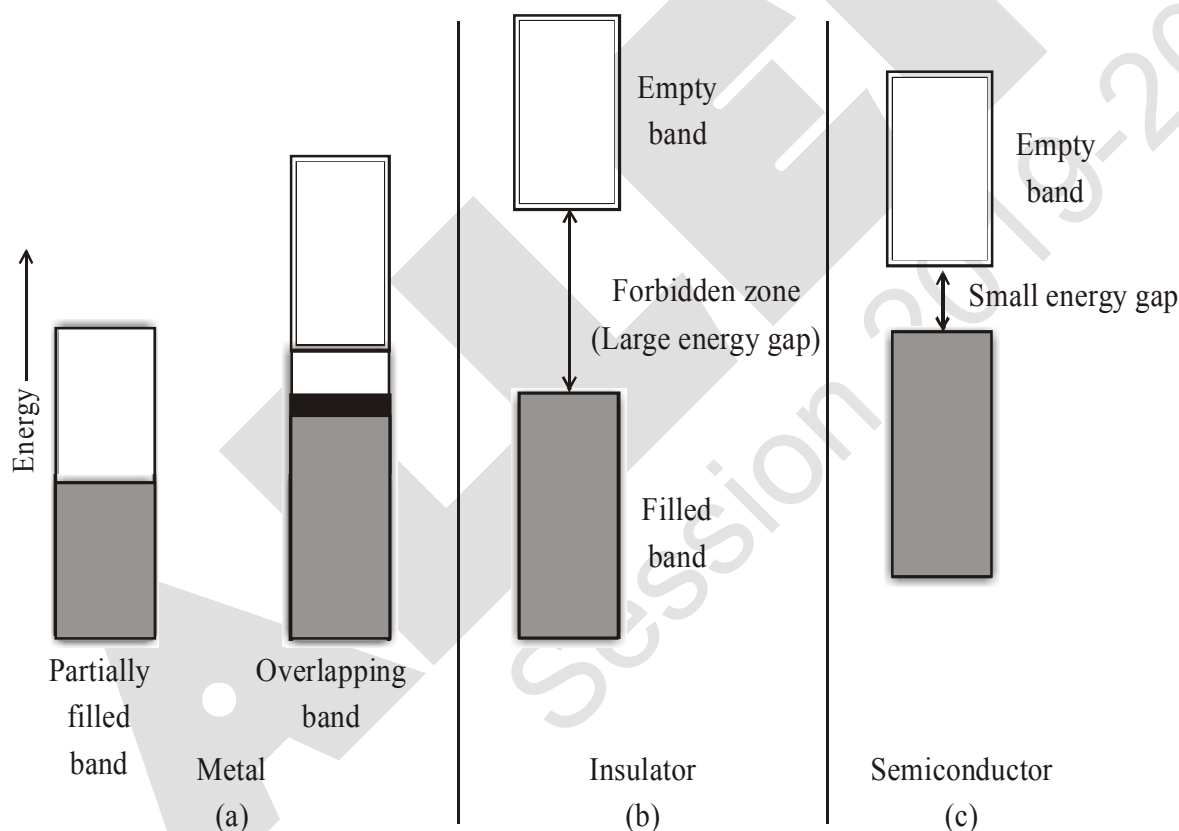
Metals conduct electricity in solid as well as molten state. The conductivity of metals depend upon the number of valence electrons available per atom. The atomic orbitals of metal atoms from molecular orbitals which are so close in energy to each other as to form a band. If this band is partially filled or it overlaps with a higher energy unoccupied conduction band, then electrons can flow easily under an applied electric field and the metal shows conductivity.

## 12.2 : Insulator :

If the gap between filled valence band and the next higher unoccupied band (conduction band) is large, electron cannot jump to it and such a substance has very small conductivity and it behaves as an insulator.

## 12.3 : Conduction of Electricity in Semi-conductor

In case of semiconductors, the gap between the valence band and conduction band is small. Therefore, some electrons may jump to conduction band and show some conductivity. Electrical conductivity of semiconductors increases with rise in temperature, since more electrons can jump to the conduction band. Substances like silicon and germanium show this type of behaviour and are called **intrinsic semiconductors**.



**Distinction among (a) metals (b) insulators and (c) semiconductors.**

**In each case, an unshaded area represents a conduction band.**

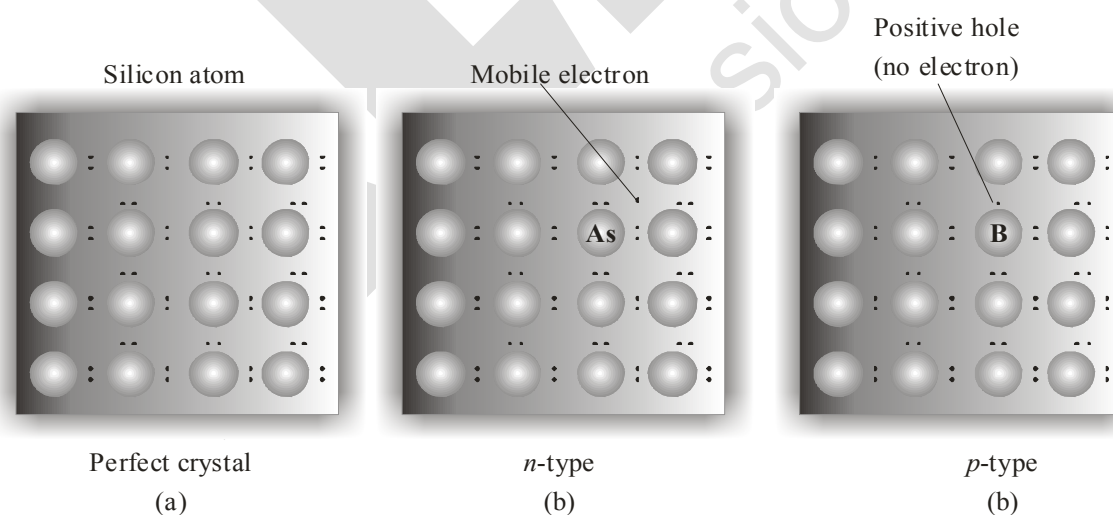
The conductivity of these intrinsic semiconductors is too low to be of practical use. Their conductivity is increased by adding an appropriate amount of suitable impurity. This process is called **doping**. Doping can be done with an impurity which is electron rich or electron deficient as compared to the intrinsic semiconductor silicon or germanium. Such impurities introduce **electrical defect** in them.

## (a) Electron – rich impurities

Silicon and germanium belong to group 14 of the periodic table and have four valence electrons each. In their crystals each atom forms four covalent bonds with its neighbours. When doped with a group 15 element like P or As, which contains five valence electrons, they occupy some of the lattice sites in silicon or germanium crystal. Four out of five electrons are used in the formation of four covalent bonds with the four neighbouring silicon atoms. The fifth electron is extra and becomes delocalised. These delocalised electrons increase the conductivity of doped silicon (or germanium). Here the increase in conductivity is due to the negatively charged electron, hence silicon doped with electron-rich impurity is called ***n-type semiconductor***.

## (b) Electron – deficit impurities

Silicon or germanium can also be doped with a group 13 element like B, Al or Ga which contains only three valence electrons. The place where the fourth valence electron is missing is called ***electron hole or electron vacancy***. An electron from a neighbouring atom can come and fill the electron hole, but in doing so it would leave an electron hole at its original position. If it happens, it would appear as if the electron hole has moved in the direction opposite to that of the electron that filled it. Under the influence of electric field, electrons would move towards the positively charged plate through electronic holes, but it would appear as if electron holes are positively charged and are moving towards negatively charged plate. This type of semi conductors are called ***p-type semiconductors***.



***Creation of n-type and p-type semi conductors by doping groups 13 and 15 elements***

**(c) Applications of n-type and p-type semiconductors**

Various combinations of *n*-type and *p*-type semiconductors are used for making electronic components. Diode is a combination of *n*-type and *p*-type semiconductor and is used as a rectifier. Transistors are made by sandwiching a layer of one type of semiconductor between two layers of the other type of semiconductor. *npn* and *pnp* type of transistors are used to detect or amplify radio or audio signals. The solar cell is an efficient photo-diode used for conversion of light energy into electrical energy.

Germanium and Silicon are group 14 elements and therefore, have a characteristic valency of four and form four bonds as in diamond. A large variety of solid state materials have been prepared by combination of group 13 and 15 or 12 and 16 to simulate average valence of four as in Ge or Si. Typical compounds of groups 13-15 are InSb, AlP and GaAs. Gallium arsenide (GaAs) semiconductor have very fast response and have revolutionised the design of semiconductor devices. ZnS, CdS, CdSe and HgTe are examples of groups 12-16 compounds. In these compounds, the bonds are not perfectly covalent and the ionic character depends on the electronegativities of the two elements.

It is interesting to learn that transition metal oxides show marked differences in electrical properties. TiO, CrO<sub>2</sub> and ReO<sub>3</sub> behave like metals. Rhenium oxide, ReO<sub>3</sub> is like metallic copper in its conductivity and appearance. Certain other oxides like VO, VO<sub>2</sub>, VO<sub>3</sub> and TiO<sub>3</sub> show metallic or insulating properties depending on temperature.

**13. MAGNETIC PROPERTIES :**

Every substance has some magnetic properties associated with it. The origin of these properties lies in the electrons. Each electron in an atom behaves like a tiny magnet. Its magnetic moment originates from two types of motions (i) its orbital motion around the nucleus and (ii) its spin around its own axis. Electron being a charged particle and undergoing these motions can be considered as a small loop of current which possesses a magnetic moment. Thus, each electron has a permanent spin and an orbital magnetic moment associated with it. Magnitude of this magnetic moment is very small and is measured in the unit called Bohr magneton,  $\mu_B$ . It is equal to  $9.27 \times 10^{-24} \text{ A m}^2$ .

On the basis of their magnetic properties, substances can be classified into five categories: (i) paramagnetic (ii) diamagnetic (iii) ferromagnetic (iv) antiferromagnetic and (v) ferrimagnetic.

**(i) Paramagnetism :**

Paramagnetic substances are weakly attracted by a magnetic field. They are magnetised in a magnetic field in the same direction. They lose their magnetism in the absence of magnetic field. Paramagnetism is due to presence of one or more unpaired electrons which are attracted by the magnetic field. O<sub>2</sub>, Cu<sup>2+</sup>, Fe<sup>3+</sup>, Cr<sup>3+</sup> are some examples of such substances.

**(ii) Diamagnetism :**

Diamagnetic substances are weakly repelled by a magnetic field. H<sub>2</sub>O, NaCl and C<sub>6</sub>H<sub>6</sub> are some examples of such substances. They are weakly magnetised in a magnetic field in opposite direction. Diamagnetism is shown by those substances in which all the electrons are paired and there are no unpaired electrons. Pairing of electrons cancels their magnetic moments and they lose their magnetic character.

(iii) **Ferromagnetism :**

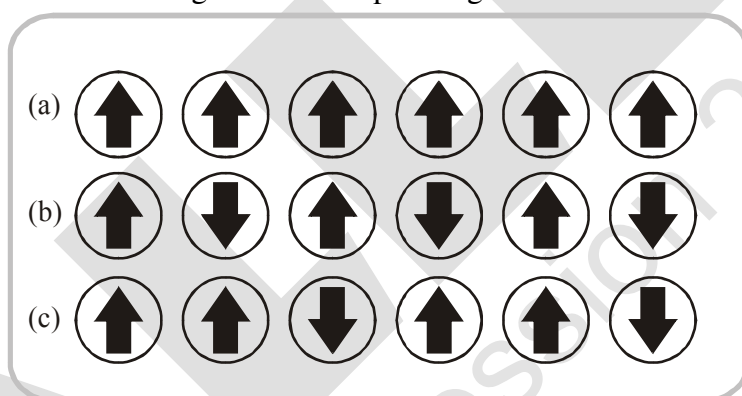
A few substances like iron, cobalt, nickel, gadolinium and  $\text{CrO}_2$  are attracted very strongly by a magnetic field. Such substances are called ferromagnetic substances. Besides strong attractions, these substances can be permanently magnetised. In solid state, the metal ions of ferromagnetic substances are grouped together into small regions called **domains**. Thus, each domain acts as a tiny magnet. In an unmagnetised piece of a ferromagnetic substance the domains are randomly oriented and their magnetic moments get cancelled. When the substance is placed in a magnetic field all the domains get oriented in the direction of the magnetic field and a strong magnetic effect is produced. This ordering of domains persists even when the magnetic field is removed and the ferromagnetic substance becomes a permanent magnet.

(iv) **Antiferromagnetism :**

Substances like  $\text{MnO}$  showing antiferromagnetism have domain structure similar to ferromagnetic substance, but their domains are oppositely oriented and cancel out each other's magnetic moment

(v) **Ferrimagnetism :**

Ferrimagnetism is observed when the magnetic moments of the domains in the substance are aligned in parallel and anti-parallel directions in unequal numbers. They are weakly attracted by magnetic field as compared to ferromagnetic substances.  $\text{Fe}_3\text{O}_4$  (magnetite) and ferrites like  $\text{MgFe}_2\text{O}_4$  and  $\text{ZnFe}_2\text{O}_4$  are examples of such substances. These substances also lose ferrimagnetism on heating and become paramagnetic.



Schematic alignment of magnetic moments in (a) ferromagnetic  
(b) antiferromagnetic and (c) ferrimagnetic

## EXERCISE : S-I

## METALLIC CRYSTALS

## Cubic crystals

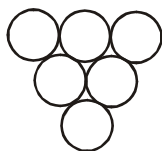
1. A closed packed structure of uniform spheres has the edge length of 600 pm. Calculate the radius of sphere, if it exist in ( $\sqrt{2} = 1.4, \sqrt{3} = 1.7$ )  
(a) simple cubic lattice (b) BCC lattice (c) FCC lattice
2. Xenon crystallises in the face-centred cubic lattice and the edge length of the unit cell is  $438\sqrt{2}$  pm. What is the nearest neighbour distance and what is the radius of xenon atom?
3. The effective radius of the iron atom is  $\sqrt{2}$  Å. It has FCC structure. Calculate its density (Fe = 56 amu,  $N_A = 6 \times 10^{23}$ )
4. Calculate the ratio of densities if same element undergoes fcc as well as simple cubic packing. Assume same atomic radius in both crystals.
5. Potassium has body-centred cubic structure with the nearest neighbour distance  $260\sqrt{3}$  pm. Its density would be ( $\frac{1}{(5.2)^2} = 0.036$ ,  $N_A = 6 \times 10^{23}$ , K = 39)
6. A cubic solid is made up of two elements 'A' and 'B'. Atoms 'B' are at the corners of the cube and 'A' at the body centre. What is the simplest formula of compound?
7. An element 'X' crystallizes in bcc. Find volume of unit cell in  $(\text{Å})^3$ , if atomic radius is  $\sqrt{3}$  Å.
8. A lattice has simple cube unit cell then number of faces which meets at a corner of a cube in this lattice is.
9. How many next nearest neighbours does potassium have in bcc lattice?
10. Number of crystal systems having, only 2 types of Bravais lattices = x,  
Number of crystal systems having, atleast 2 interfacial angles equal = y,  
all the three interfacial angles and all the three axes lengths equal = z  
Then find  $y - (x + z)$ .

## PACKING IN SOLIDS

11. A cubic solid is made by atoms 'A' forming close pack arrangement, 'B' occupying one-fourth of tetrahedral void and C occupying half of the octahedral voids. What is the formula of compound?
12. If number of nearest neighbours, next nearest ( $2^{\text{nd}}$  nearest) neighbour and next to next nearest ( $3^{\text{rd}}$  nearest) neighbours are x, y and z respectively for body centred cubic unit cell, then calculate value of  $\frac{xy}{z}$  is.
13. In FCC unit cell, what fraction of edge is not covered by atoms?
14. Element A crystallizes in hcp. Calculate total number of tetrahedral voids in 24 micrograms of A ( $N_A = 6 \times 10^{23}$ , Atomic mass of A = 48)
15. For ABC ABC ABC .... packing, distance between two successive tetrahedral void is X and distance between two successive octahedral void is y in an unit cell, then  $\frac{y\sqrt{2}}{X}$  is



16. An element 'M' crystallizes in ABAB....type packing. If adjacent layer A & B are  $10\frac{\sqrt{2}}{\sqrt{3}}$  pm apart, then calculate radius of largest sphere which can be fitted in the void without disturbing the lattice arrangement (Given :  $\sqrt{2} = 1.414$ )
17. A 3d unit cell is such that one of its planes has the following arrangement of atoms.



What will be the number of next nearest neighbour in such unit cell?

18. The density of solid Argon is 1.6 gm/ml at  $-233^\circ\text{C}$ . If the atomic volume of Argon is assumed to be  $\frac{5}{3} \times 10^{-23} \text{ cm}^3$  then what % of solid Argon is apparently empty space ? ( $\text{Ar} = 40$ ,  $N_A = 6 \times 10^{23}$ )
19. An element crystallizes in a structure having FCC unit cell of an edge 200 pm. Calculate the density, if 200 g of this element contains  $2.4 \times 10^{24}$  atoms. ( $N_A = 6 \times 10^{23}$ )
20. Find packing fraction of three dimensional unit cell of AAAAAA.....type hypothetical arrangement in which hexagonal packing is taken in layer.

### IONIC CRYSTALS

21. If the radius of  $\text{Mg}^{2+}$  ion,  $\text{Cs}^+$  ion,  $\text{O}^{2-}$  ion,  $\text{S}^{2-}$  ion and  $\text{Cl}^-$  ion are 0.65 Å, 1.69 Å, 1.40 Å, 1.84 Å, and 1.81 Å respectively, calculate the co-ordination numbers of the cations in the crystals of  $\text{MgS}$ ,  $\text{MgO}$  and  $\text{CsCl}$ .
22. The two ions  $\text{A}^+$  and  $\text{B}^-$  have radii 88 pm and 200 pm respectively. In the closed packed crystal of compound AB, predict the co-ordination number of  $\text{A}^+$ .
23. Spinel is a important class of oxides consisting of two types of metal ions with the oxide ions arranged in CCP pattern. The normal spinel has one-eight of the tetrahedral holes occupied by one type of metal ion and one half of the octahedral hole occupied by another type of metal ion. Such a spinel is formed by  $\text{Zn}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{O}^{2-}$ , with  $\text{Zn}^{2+}$  in the tetrahedral holes. Give the formula of spinel.
24. KF crystallizes in the NaCl type structure. If the radius of  $\text{K}^+$  ion is 132 pm and that of  $\text{F}^-$  ion is 135 pm, what is the shortest K–F distance? What is the edge length of the unit cell? What is the closet  $\text{K}^+ - \text{K}^+$  distance?
25.  $\text{CsCl}$  has bcc unit cell with edge length 400 pm. Calculate the interionic distance in  $\text{CsCl}$ .
26. The density of KBr is  $2.38 \text{ g cm}^{-3}$ . The length of the edge of the unit cell is 700 pm. Find the number of formula unit of KBr present in the single unit cell. ( $N_A = 6 \times 10^{23} \text{ mol}^{-1}$ , At. mass : K = 39, Br = 80)

27. A crystal of lead(II) sulphide has NaCl structure. In this crystal the shortest distance between  $\text{Pb}^{+2}$  ion and  $\text{S}^{2-}$  ion is 300 pm. What is the length of the edge of the unit cell in lead sulphide? Also calculate the unit cell volume.
28. If the length of the body diagonal for CsCl which crystallises into a cubic structure with  $\text{Cl}^-$  ions at the corners and  $\text{Cs}^+$  ions at the centre of the unit cell, is 7 Å and the radius of the  $\text{Cs}^+$  ion is 1.69 Å, what is the radius of  $\text{Cl}^-$  ion?
29. RbI crystallizes in (8 : 8) structure in which each  $\text{Rb}^+$  is surrounded by eight iodide ions each of radius 2.17 Å. Find the length of one side of RbI unit cell, assuming anion, anion contact.
30. Solid AB has NaCl type structure. If the radius of  $\text{A}^+$  and  $\text{B}^-$  are 0.8 Å and 1.2 Å respectively and formula mass of AB is 48 g/mole, what is the density of AB solid.

Take : Avogadro's number =  $6 \times 10^{23}$

### PROBLEMS RELATED WITH DEFECTS IN SOLID

31. The composition of a sample of wustite is  $\text{Fe}_{0.93}\text{O}_{1.0}$ . What percentage of iron is present in the form of Fe(III)?
32. If NaCl is doped with  $10^{-3}$  mol %  $\text{SrCl}_2$ , what is the number of cation vacancies per mole of NaCl? ( $N_A = 6 \times 10^{23}$ )
33. AgCl has the same structure as that of NaCl. The edge length of unit cell of AgCl is found to be 523.5 pm and the density of AgCl is  $6.0 \text{ g cm}^{-3}$ . Find the percentage of sites that are unoccupied.  
[ $\text{Ag} = 108$ ,  $(5.235)^3 = 143.5$ ]
34. A non stoichiometric compound  $\text{Fe}_7\text{S}_8$  consist of iron in both  $\text{Fe}^{+2}$  and  $\text{Fe}^{+3}$  form and sulphur is present as sulphide ions. Calculate cation vacancies as a percentage of  $\text{Fe}^{+2}$  initially present in the ideal crystal.
35. The density of ZnS crystal (Zinc blende structure) having 10% Frenkel defect is  
[  $r_{\text{Zn}^{2+}} = 40\sqrt{3}\text{pm}$ ,  $r_{\text{S}^{2-}} = 110\sqrt{3}\text{pm}$ ,  $\text{Zn} = 65.2$ ,  $\text{S} = 32$  ]

## EXERCISE : S-II

1. An element (atomic weight = 125) crystallises in simple cubic structure. Diameter of the largest atom which can be placed without disturbing unit cell is 366 pm. If the density of element 'x'  $\text{gm/cm}^3$ , the value of

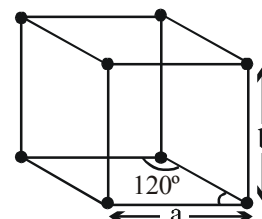
$$\left(\frac{6x}{5}\right) \text{ is}$$

[Given :  $\sqrt{3} = 1.732$ ,  $N_A = 6 \times 10^{23}$ ]

2. The density of diamond from the fact that it has face centred cubic structure with two atoms per lattice point and unit cell edge length of  $3.6 \text{ \AA}$ , is 'x'  $\text{gm/cm}^3$ , then the value of  $(1.458x)$  is ( $N_A = 6 \times 10^{23}$ )
3. Iron crystallizes in several modifications. At about  $910^\circ\text{C}$ , the body-centred cubic ' $\alpha$ ' form undergoes a transition to the face-centred cubic ' $\gamma$ ' form. Assuming that the distance between nearest neighbours is the same in the two forms at the transition temperature, the ratio of the density of  $\gamma$  iron to that of  $\alpha$  iron at the transition temperature,  $x : 1$ , then the value of  $(3\sqrt{6}x)$  is.
4. What is the percent by mass of titanium in rutile, a mineral that contain titanium and oxygen, if structure can be described as a closest packed array of oxide ions, with titanium in one half of the octahedral holes. What is the oxidation number of titanium? ( $\text{Ti} = 48$ )
5. An element crystallizes into a structure which may be described by a cubic type of unit cell having one atom on each corner of the cube and two extra atoms on one of its body diagonal. If the volume of this unit cell is  $2.4 \times 10^{-23} \text{ cm}^3$  and density of element is  $7.2 \text{ g cm}^{-3}$ , calculate the number of atoms present in 288 g of element.
6. What will be packing fraction of solid in which atoms are present at corners and cubic void is occupied. The insertion of the sphere into void does not disturb simple cubic lattice.
7. Ice crystallizes in a hexagonal lattice. At the low temperature at which the structure was determined,

the lattice constants where  $a = 5 \text{ \AA}$ , and  $b = 3.5\sqrt{3} \text{ \AA}$

How many molecules are contained in the given unit cell?



$$[\text{density (ice)} = \frac{16}{17.5} \text{ gm/cm}^3]$$

8. The mineral hawleyite, one form of  $\text{CdS}$ , crystallizes in one of the cubic lattices, with edge length  $5.87 \text{ \AA}$ . The density of hawleyite is  $4.63 \text{ g cm}^{-3}$ . ( $\text{Cd} = 112$ )
- (i) In which cubic lattice does hawleyite crystallize?
- (ii) Find the Schottky defect in  $\text{g cm}^{-3}$ .
9.  $\text{KCl}$  crystallizes in the same type of lattice as does  $\text{NaCl}$ . Given that  $\frac{r_{\text{Na}^+}}{r_{\text{Cl}^-}} = 0.5$  and  $\frac{r_{\text{Na}^+}}{r_{\text{K}^+}} = 0.7$  Calculate:
- (a) The ratio of the sides of unit cell for  $\text{KCl}$  to that for  $\text{NaCl}$  and

$$\left( \left( \frac{8}{7} \right)^3 = 1.5, \frac{74.5}{58.5} = 1.25 \right)$$

10. A cubic unit cell contains manganese ions at the corners and fluoride ions at the center of each edge.
  - (a) What is the empirical formula of the compound?
  - (b) What is the co-ordination number of the Mn ion?
  - (c) Calculate the edge length of the unit cell, if the radius of Mn ion is  $0.65 \text{ \AA}$  and that of  $\text{F}^-$  ion is  $1.36 \text{ \AA}$ .
11. Potassium crystallizes in a body-centred cubic lattice with edge length,  $a = 5.2 \text{ \AA}$ .
  - (a) What is the distance between nearest neighbours?
  - (b) What is the distance between next-nearest neighbours?
  - (c) How many nearest neighbours does each K atom have?
  - (d) How many next-nearest neighbours does each K atom have?
  - (e) What is the density of crystalline potassium?(Given :  $K = 39$ ,  $(5.2)^3 = 140$ )
12. An element X (atomic weight =  $24 \text{ gm/mole}$ ) forms a face centred cubic lattice. If the edge length of the lattice is  $4 \times 10^{-8} \text{ cm}$  and the observed density is  $2.40 \times 10^3 \text{ kg/m}^3$ , calculate the percentage occupancy of lattice points by X element. (Given :  $N_A = 6 \times 10^{23}$ )
13. Calculate the density (in  $\text{gm/cm}^3$ ) of NaCl type ionic solid ( $\text{MW} = 75 \text{ gm/mol}$ ) if distance between two nearest cations is  $250\sqrt{2} \text{ pm}$  (avogadro number =  $6 \times 10^{23}$ )
14. The olivine series of minerals consists of crystals in which Fe and Mg ions may substitute for each other causing substitutional impurity defect without changing the volume of the unit cell. In olivine series of minerals, oxide ion exist as FCC with  $\text{Si}^{4+}$  occupying  $1/4$  th of octahedral voids and divalent ions occupying  $1/4$ th of tetrahedral voids. The density of forsterite (magnesium silicate) is  $3.0 \text{ g/cc}$  and that of fayalite (ferrous silicate) is  $4.0 \text{ g/cc}$ . Find the formula of forsterite and fayalite minerals and the mass percentage of fayalite in an olivine with a density of  $3.5 \text{ g/cc}$ .

## EXERCISE : O-I

## SINGLE CORRECT :

- Which of the following are the correct axial distances and axial angles for rhombohedral system ?  
 (A)  $a = b = c, \alpha = \beta = \gamma \neq 90^\circ$  (B)  $a = b \neq c, \alpha = \beta = \gamma = 90^\circ$   
 (C)  $a \neq b = c, \alpha = \beta = \gamma = 90^\circ$  (D)  $a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$
- $a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$  represents  
 (A) tetragonal system (B) orthorhombic system  
 (C) monoclinic system (D) triclinic system
- Diamond belongs to the crystal system :  
 (A) Cubic (B) triclinic (C) tetragonal (D) hexagonal
- A match box exhibits -  
 (A) Cubic geometry (B) Monoclinic geometry  
 (C) Tetragonal geometry (D) Orthorhombic geometry
- Which of the following solids substances will have same refractive index when measured in different directions?  
 (A) NaCl (B) Monoclinic sulphur (C) Rubber (D) Graphite
- In the body-centred cubic unit cell & face centred cubic unit cell, the radius of atom in terms of edge length(a) of the unit cell is respectively:  
 (A)  $\frac{a}{2}, \frac{a}{2\sqrt{2}}$  (B)  $\frac{a}{2\sqrt{2}}, \frac{\sqrt{3}a}{4}$  (C)  $\frac{\sqrt{3}a}{4}, \frac{a}{2\sqrt{2}}$  (D)  $\frac{\sqrt{3}a}{2}, \frac{a}{2\sqrt{2}}$
- Crystal system in which maximum number of Bravais lattices are possible is  
 (A) Cubic (B) Triclinic (C) Orthorhombic (D) Rhombohedral
- Number of atoms at second nearest position from a given atom in a BCC structure is  
 (A) 8 (B) 6 (C) 12 (D) 4
- Percentage area of each face covered by atoms in a FCC unit cell is -  
 (A) 60.4% (B) 68% (C) 74% (D) 78.5%
- Correct sequence of the coordination number in SC, FCC & BCC is-  
 (A) 6, 8, 12 (B) 6, 12, 8 (C) 8, 12, 6 (D) 8, 6, 12
- If 'Z' is the number of atoms in the unit cell that represents the closest packing sequence ---A B C A B C ---, the number of tetrahedral voids in the unit cell is equal to  
 (A) Z (B) 2Z (C) Z/2 (D) Z/4
- The interstitial hole is called tetrahedral because  
 (A) It is formed by four spheres.  
 (B) Partly same and partly different.  
 (C) It is formed by four spheres the centres of which form a regular tetrahedron.  
 (D) None of the above three.
- The size of an octahedral void formed in a closest packed lattice as compared to tetrahedral void is  
 (A) Equal (B) Smaller (C) Larger (D) Not definite

14. If the anions (A) form hexagonal closest packing and cations (C) occupy only  $\frac{2}{3}$  octahedral voids in it, then the general formula of the compound is  
 (A) CA (B)  $CA_2$  (C)  $C_2A_3$  (D)  $C_3A_2$
15. Which one of the following schemes of ordering closest packed sheets of equal sized spheres do not generate close packed lattice.  
 (A) ABCABC (B) ABACABAC (C) ABBAABBA (D) ABCBCABCBC
16. Copper metal crystallizes in FCC lattice. Edge length of unit cell is 362 pm. The radius of largest atom that can fit into the voids of copper lattice without disturbing it is  
 (A) 53 pm (B) 45 pm (C) 93 pm (D) 87 pm
17. Packing fraction in 2-D hexagonal arrangement of identical sphere is  
 (A)  $\frac{\pi}{3\sqrt{2}}$  (B)  $\frac{\pi}{3\sqrt{3}}$  (C)  $\frac{\pi}{2\sqrt{3}}$  (D)  $\pi/6$
18. In fcc unit cell smallest distance between octahedral void & tetrahedral void is -  
 (a = edge length of unit cell )  
 (A)  $\frac{a}{\sqrt{2}}$  (B)  $\frac{\sqrt{3}a}{2}$  (C) a (D)  $\frac{\sqrt{3}a}{4}$
19. What is not true regarding hexagonal close packing (hcp)  
 (A) packing fraction is 0.74  
 (B) coordination number is 12  
 (C) ABC ABC.....type packing  
 (D) Containing both tetrahedral and octahedral voids
20. In which of the following arrangement distance between two nearest neighbours is maximum, considering identical sized atoms in all arrangements ?  
 (A) Simple cubic (B) bcc (C) fcc (D) equal in all
21. How many unit cell are there in 1 gram cubic crystal of NaCl ?  
 (A)  $\frac{4 \times N_A}{58.5}$  (B)  $\frac{N_A}{58.5}$  (C)  $\frac{N_A}{58.5 \times 4}$  (D)  $\frac{N_A}{58.5 \times 8}$
22. The density of  $CaF_2$  (fluorite structure) is  $3.18 \text{ g/cm}^3$ . The length of the side of the unit cell is (Ca = 40, F = 19)  
 (A) 253 pm (B) 344 pm (C) 546 pm (D) 273 pm
23. The coordination number of cation and anion in Fluorite  $CaF_2$  and CsCl are respectively  
 (A) 8:4 and 6:3 (B) 6:3 and 4:4 (C) 8:4 and 8:8 (D) 4:2 and 2:4
24. A compound XY crystallizes in 8 : 8 lattice with unit cell edge length of 480 pm. If the radius of  $Y^-$  is 225 pm, then the radius of  $X^+$  is  
 (A) 127.5 pm (B) 190.68 pm (C) 225 pm (D) 255 pm
25. The mass of a unit cell of CsCl corresponds to  
 (A) 1  $Cs^+$  and 1  $Cl^-$  (B) 1  $Cs^+$  and 6  $Cl^-$  (C) 4  $Cs^+$  and 4  $Cl^-$  (D) 8  $Cs^+$  and 1  $Cl^-$

26. An ionic compound AB has ZnS type structure. If the radius  $A^+$  is 22.5 pm, then the ideal radius of  $B^-$  would be  
 (A) 54.35 pm (B) 100 pm (C) 145.16 pm (D) none of these
27. Edge length of  $M^+X^-$  (NaCl structure) is 7.2 Å. Assuming  $M^+ - X^-$  contact along the cell edge, radius of  $X^-$  ion is ( $r_{M^+} = 1.6 \text{ Å}$ ) :  
 (A) 2.0 Å (B) 5.6 Å (C) 2.8 Å (D) 38 Å
28.  $NH_4Cl$  crystallizes in CsCl type lattice with a unit cell edge length of 387 pm. The distance between the oppositely charged ions in the lattice is  
 (A) 335.1 pm (B) 83.77 pm (C) 274.46 pm (D) 137.23 pm
29.  $r_{Na^+} = 95 \text{ pm}$  and  $r_{Cl^-} = 181 \text{ pm}$  in NaCl (rock salt) structure. What is the shortest distance between  $Na^+$  ions?  
 (A) 778.3 pm (B) 276 pm (C) 195.7 pm (D) 390.3 pm
30. AB crystallises itself as NaCl crystal. If  $r_+ = \frac{2}{\sqrt{6}}$  and  $r_- = \sqrt{6}$ , the edge length of cube is  
 (A)  $2\sqrt{3}$  (B)  $\frac{4}{\sqrt{3}}$  (C)  $\frac{8}{\sqrt{6}}$  (D)  $\frac{16}{\sqrt{6}}$
31. Which of the following is the most likely to show schottky defect ?  
 (A)  $CaF_2$  (B) ZnS (C) AgCl (D) CsCl
32. In the Schottky defect, in AB type ionic solids  
 (A) cations are missing from the lattice sites and occupy the interstitial sites  
 (B) equal number of cations and anions are missing  
 (C) anions are missing and electrons are present in their place  
 (D) equal number of extra cations and electrons are present in the interstitial sites
33. Choose the correct option.  
 (A) Two adjacent face centre atom doesn't touch each other in fcc unit cell because they are not nearest atom of face each other in fcc lattice  
 (B) Number of nearest  $Na^+$  ions of another  $Na^+$  in  $Na_2O$  crystal will be 24.  
 (C) Minimum distance between two cubical voids in simple cube unit cell lattice will be 'a' where 'a' is length of edge of unit cell  
 (D) By defects in solids, density of solids either remains constant or decreases but it can never increase.
34. The measured density of AgI is  $6.94 \text{ g/cm}^{-3}$  and the theoretical density is  $5.67 \text{ g/cm}^{-3}$ . These data indicate that solid AgI has -  
 (A) Schottky defect (B) Frenkel defect  
 (C) Interstitial impurities defect (D) Both (1) and (2)
35. Which of the following statement is **CORRECT** ?  
 (A) A metal can show only non- stoichiometric defects  
 (B) Schottky defect reduces the density of a solid due to significant increase in volume.  
 (C) Impurity defect always change the density.  
 (D) Solids having F-centres may have metal excess defect due to missing anions.

### ***EXERCISE : O-II***

***SINGLE CORRECT :***

- The only incorrect statement for the packing of identical spheres in two dimension is :
  - For square close packing , coordination number is 4.
  - For hexagonal close packing, coordination number is 6.
  - There is only one void per atom in both, square and hexagonal close packing.
  - Hexagonal close packing is more efficiently packed than square close packing.
- Correct statement for ccp is :
  - Each octahedral void is surrounded by 6 spheres and each sphere is surrounded by 4 octahedral voids
  - Each octahedral void is surrounded by 6 spheres and each sphere is surrounded by 6 octahedral voids
  - Each octahedral void is surrounded by 6 spheres and each sphere is surrounded by 8 octahedral voids
  - Each octahedral void is surrounded by 6 spheres and each sphere is surrounded by 12 octahedral voids
- Which of the following statements is correct in the rock-salt structure of an ionic compounds?
  - coordination number of cation is four whereas that of anion is six.
  - coordination number of cation is six whereas that of anion is four.
  - coordination number of each cation and anion is four.
  - coordination number of each cation and anion is six.

***MORE THAN ONE MAY BE CORRECT :***

4. Which of the following statements is/are correct :
  - (A) In an anti-fluorite structure, anions form FCC lattice and cations occupy all tetrahedral voids.
  - (B) If the radius of cations and anions are  $0.2 \text{ \AA}$  and  $0.95 \text{ \AA}$  , then coordination number of cation in the crystal is 4.
  - (C) Each sphere is surrounded by six voids in two dimensional hexagonal close packed layer.
  - (D) 8  $\text{Cs}^+$  ions occupy the second nearest neighbour locations of a  $\text{Cs}^+$  ion in  $\text{CsCl}$  crystals.
5. Select correct statement(s)
  - (A) Density of crystal always increases due to substitutional impurity defect.
  - (B) An ion is transferred from a lattice site to an interstitial position in Frenkel defect.
  - (C) In  $\text{AgCl}$ , the silver ion is displaced from its lattice position to an interstitial position. Such a defect is called a frenkel defect
  - (D) None
6. Lead metal has a density of  $11.34 \text{ g/cm}^3$  and crystallizes in a face-centred lattice. Choose the correct alternatives ( $\text{Pb} = 208$  ,  $N_A = 6 \times 10^{23}$ )
  - (A) the volume of one unit cell is  $1.22 \times 10^{-22} \text{ cm}^3$ .
  - (B) the volume of one unit cell is  $1.22 \times 10^{-19} \text{ cm}^3$ .
  - (C) the atomic radius of lead is  $175 \text{ pm}$ .
  - (D) the atomic radius of lead is  $155.1 \text{ pm}$ .



7. Which of the following statement(s) is/are correct ?
- (A) NaCl is a 'AB' crystal lattice that can be interpreted to be made up of two individual fcc unit cells of  $A^+$  and  $B^-$  fused together in such a manner that the corner of one unit cell becomes the edge centre of the other.
- (B) In a face centred cubic unit cell, the body centre is an octahedral void.
- (C) In fcc unit cell, octahedral and tetrahedral voids are equal in number.
- (D) Tetrahedral voids =  $2 \times$  octahedral voids, is valid for ccp and hcp.
8. Select the correct statement (s) :
- (A) CsCl mainly shows Schottky defect (B) ZnS mainly shows Frenkel defect
- (C) NaCl unit cell contain  $4Na^+$  and  $4Cl^-$  (D) Truncated octahedron have 24 corners.
9. Select the correct statement(s) –
- (A) The ionic crystal of AgBr has Schottky defect.
- (B) The unit cell having crystal parameters,  $a = b \neq c$ ,  $\alpha = \beta = 90^\circ$ ,  $\gamma = 120^\circ$  is hexagonal
- (C) Ionic compounds having Frenkel defect has high  $r^+/r^-$  ratio.
- (D) The co-ordination number of  $Na^+$  ion in NaCl is 6
10. Which of the following is/are true ?
- (A) Ratio of nearest neighbours in simple cubic cell to next nearest neighbours in face centred is cubic cell is 1.
- (B) Packing efficiency of a unit cell in which atoms are present at each corner and each edge centre is about 26 % in metallic crystal.
- (C) Distance between two planes in FCC or HCP arrangement is same for a metal existing in both forms, with same atomic radius.
- (D) If number of unit cell along one edge are 'x', then total number of unit cell in cube =  $x^3$

**ASSERTION / REASON :**

11. **Statement-1** : In Antifluorite structure ( $Li_2O$ ), the oxide ions occupy c.c.p. (cubic close packing) and  $Li^+$  ions, 100% tetrahedral voids.

**Statement-2** : The distance of the nearest neighbours in antifluorite structure is  $\frac{\sqrt{3}a}{4}$ , where 'a' is the edge length of the cube

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
- (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
- (C) Statement-1 is true, statement-2 is false.
- (D) Statement-1 is false, statement-2 is true.
12. **Statement-1** : In FCC unit cell, packing efficiency is more when all tetrahedral voids are filled with spheres of maximum possible size as compared with packing efficiency when all octahedral voids are filled in similar way.
- Statement-2** : Tetrahedral voids are more in the number than octahedral voids in FCC.
- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
- (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
- (C) Statement-1 is true, statement-2 is false.
- (D) Statement-1 is false, statement-2 is true.

13. **Statement-1:** In diamond, carbon atoms occupy alternate tetrahedral voids in the FCC lattice formed by the carbon atoms.  
**कथन-2:** In diamond, packing fraction is more than 74%.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.
14. **Statement-1 :** Due to Frenkel defect, there is no effect on the density of the crystalline solid.  
**Statement-2 :** In Frenkel defect, no cation or anion leaves the crystal.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.
15. **Statement-1 :** Conductivity of silicon increased by doping it with group 15 element.  
**Statement-2 :** Doping means introduction of small amount of impurities like P or As into pure silicon crystal.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

**COMPREHENSION :**

**Paragraph for Q.16 & Q.17**

Solid balls of radius 17.32 cm crystallises in bcc pattern. During one such crystallisation, some oxygen gas is trapped. This trapped oxygen at 640K creates pressure of 5 atm.

**Assume :**

- (i) BCC arrangement is not disturbed due to trapping of gas.  
 (ii) Gas is uniformly distributed inside unit cell

[Take  $R = 0.08 \text{ atm-litre/mole-K}$ ,  $N_A = 6 \times 10^{23}$ , Mass of a solid ball = 64 gms]

16. Number of oxygen molecules present in an unit cell is -  
 (A)  $2.4 \times 10^{24}$  (B)  $1.2 \times 10^{24}$  (C)  $6 \times 10^{23}$  (D)  $3 \times 10^{23}$
17. Calculate percentage increase in density due to trapping of gas  
 (A) 16.67 % (B) 33.33 % (C) 100% (D) 50%

**Paragraph for (Que. 18 to 21)**

Calcium crystallizes in a cubic unit cell with density 3.2 g/cc. Edge-length of the unit cell is 437 pm.

18. The type of unit cell is  
 (A) Simple cubic (B) BCC (C) FCC (D) Edge-centred
19. The nearest neighbour distance is  
 (A) 154.5 pm (B) 309 pm (C) 218.5 pm (D) 260 pm
20. The number of nearest neighbours of a Ca atom are  
 (A) 4 (B) 6 (C) 8 (D) 12

21. If the metal is melted, density of the molten metal was found to be 3 g/cc. What will be the percentage of empty space in the molten metal?

(A) 31% (B) 36% (C) 28% (D) 49%

**TABLE TYPE COMPREHENSION :**

| Column-I                                  | Column-II                                      | Column-III                                   |
|-------------------------------------------|------------------------------------------------|----------------------------------------------|
| (A) NaCl (Rock salt) structure            | (i) Cation - FCC<br>Anion - Tetrahedral void   | (I) All tetrahedral voids are occupied       |
| (B) CsCl structure                        | (ii) Anion - FCC<br>Cation - Tetrahedral voids | (II) All octahedral voids are occupied       |
| (C) ZnS (zinc blende) structure           | (iii) Anion - SC<br>Cation - Cubic voids       | (III) 50 % of tetrahedral voids are occupied |
| (D) CaF <sub>2</sub> (fluorite) structure | (iv) Anion - FCC<br>Cation - Octahedral void   | (IV) All octahedral voids are empty          |

22. Which of the following is correct match ?

(A) A, i, I (B) A, ii, IV (C) A, iv, II (D) A, iv, IV

23. Which of the following is incorrect match ?

(A) B, iii, I (B) C, ii, III (C) D, i, I (D) D, i, IV

24. Which of the following is correct match ?

(A) D, ii, I (B) B, iv, IV (C) D, iii, I (D) C, ii, IV

**MATCH THE COLUMN :**

25. Match the column

**Column I**

- (A) Tetragonal and Hexagonal  
(B) Cubic and Rhombohedral  
(C) Monoclinic and Triclinic  
(D) Cubic and Hexagonal

**Column II**

- (P) are two crystal systems  
(Q)  $a = b \neq c$   
(R)  $a \neq b \neq c$   
(S)  $a = b = c$

26. Match the column:

**Column I**

- (A) Rock salt structure  
(B) Zinc Blend structure  
(C) Fluorite structure

**Column II**

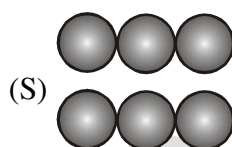
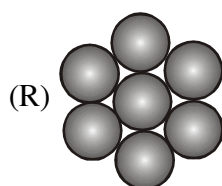
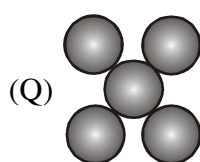
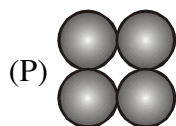
- (P) Co-ordination number of cation is 4  
(Q)  $\frac{\sqrt{3}a}{4} = r_+ + r_-$   
(R) Co-ordination number of cation and anion are same  
(S) Distance between two nearest anion is  $\frac{a}{\sqrt{2}}$

**MATCHING LIST TYPE :**

27. Match the column

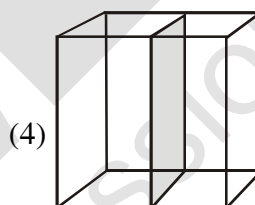
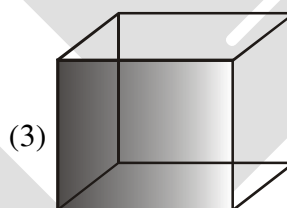
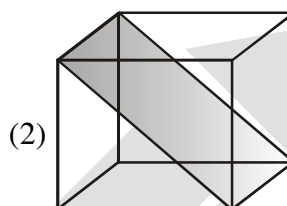
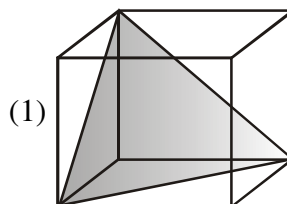
**Column I**

(Arrangement of the atoms/ions)



**Column II**

(Planes in fcc lattice)



Code :

|     | P | Q | R | S |
|-----|---|---|---|---|
| (A) | 4 | 3 | 1 | 2 |
| (B) | 4 | 3 | 2 | 1 |
| (C) | 3 | 2 | 1 | 4 |
| (D) | 1 | 2 | 4 | 3 |

| 28. | Column I                                       | Column II                                                                  |
|-----|------------------------------------------------|----------------------------------------------------------------------------|
|     | [Distance in terms of edge length of cube (a)] |                                                                            |
| (P) | 0.866 a                                        | (1) Shortest distance between cation & anion in CsCl structure.            |
| (Q) | 0.707 a                                        | (2) Shortest distance between two cation in $\text{CaF}_2$ structure.      |
| (R) | 0.433 a                                        | (3) Shortest distance between carbon atoms in diamond.                     |
| (S) | a                                              | (4) shortest distance between next nearest cations in rock salt structure. |

Code :

|     | P | Q | R | S |
|-----|---|---|---|---|
| (A) | 4 | 3 | 1 | 2 |
| (B) | 1 | 2 | 3 | 4 |
| (C) | 3 | 2 | 1 | 4 |
| (D) | 1 | 2 | 4 | 3 |

EXERCISE : J-MAIN

- The no. of atoms per unit cell in B.C.C. & F.C.C. is respectively : [AIEEE-02]  
 (1) 8, 10 (2) 2, 4 (3) 1, 2 (4) 1, 3
- How many unit cells are present in a cube-shaped ideal crystal of NaCl of mass 1.00g ? [AIEEE-03]  
 (1)  $1.28 \times 10^{21}$  unit cells (2)  $1.71 \times 10^{21}$  unit cells  
 (3)  $2.57 \times 10^{21}$  unit cells (4)  $5.14 \times 10^{21}$  unit cells
- What type of crystal defect is indicated in the diagram below ? [AIEEE-04]  

|                 |                 |                 |                 |                 |                 |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Na <sup>+</sup> | Cl <sup>-</sup> | Na <sup>+</sup> | Cl <sup>-</sup> | Na <sup>+</sup> | Cl <sup>-</sup> |
| Cl <sup>-</sup> |                 | Cl <sup>-</sup> | Na <sup>+</sup> |                 | Na <sup>+</sup> |
| Na <sup>+</sup> | Cl <sup>-</sup> |                 | Cl <sup>-</sup> | Na <sup>+</sup> | Cl <sup>-</sup> |
| Cl <sup>-</sup> | Na <sup>+</sup> | Cl <sup>-</sup> | Na <sup>+</sup> |                 | Na <sup>+</sup> |

 (1) Frenkel defect (2) Schottky defect  
 (3) Interstitial defect (4) Frenkel and Schottky defects
- An ionic compound has a unit cell consisting of A ions at the corners of a cube and B ions on the centres of the faces of the cube. The empirical formula of this compound would be- [AIEEE-05]  
 (1) A<sub>2</sub>B (2) AB (3) A<sub>3</sub>B (4) AB<sub>3</sub>
- Lattice energy of an ionic compound depends upon - [AIEEE-05]  
 (1) Size of the ion only (2) Charge on the ion only  
 (3) Charge on the ion and size of the ion (4) Packing of ions only
- Total volume of atoms present in a face-centred cubic unit cell of a metal is (r is atomic radius) : [AIEEE-06]  
 (1)  $\frac{24}{3}\pi r^3$  (2)  $\frac{12}{3}\pi r^3$  (3)  $\frac{16}{3}\pi r^3$  (4)  $\frac{20}{3}\pi r^3$
- In a compound, atoms of element Y form ccp lattice and those of element X occupy  $\frac{2}{3}$ rd of tetrahedral voids. The formula of the compound will be - [AIEEE-08]  
 (1) X<sub>4</sub>Y<sub>3</sub> (2) X<sub>2</sub>Y<sub>3</sub> (3) X<sub>2</sub>Y (4) X<sub>3</sub>Y<sub>4</sub>
- The edge length of a face centred cubic cell of an ionic substance is 508 pm. If the radius of the cation is 110 pm, the radius of the anion is :- [AIEEE-10]  
 (1) 144 pm (2) 288 pm (3) 398 pm (4) 618 pm
- Percentages of free space in cubic close packed structure and in body centred packed structure are respectively :- [AIEEE-10]  
 (1) 48% and 26% (2) 30% and 26% (3) 26% and 32% (4) 32% and 48%

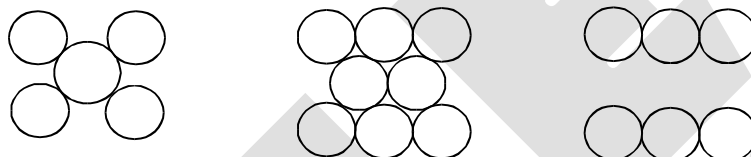
10. The radius of a calcium ion is 94 pm and of the oxide ion is 146 pm. The possible crystal structure of calcium oxide will be :- [Jee-Main (online)-12]  
(1) Octahedral (2) Tetrahedral (3) Pyramidal (4) Trigonal
11. Ammonium chloride crystallizes in a body centred cubic lattice with edge length of unit cell of 390 pm. If the size of chloride ion is 180 pm, the size of ammonium ion would be: [Jee-Main (online)-12]  
(1) 158 pm (2) 174 pm (3) 142 pm (4) 126 pm
12. A solid has 'bcc' structure. If the distance of nearest approach between two atoms is  $1.73 \text{ \AA}$ , the edge length of the cell is :- [Jee-Main (online)-12]  
(1) 314.20 pm (2) 216 pm (3) 200 pm (4) 1.41 pm
13. Among the following the incorrect statement is :- [Jee-Main (online)-12]  
(1) Density of crystals remains unaffected due to Frenkel defect  
(2) In BCC unit cell the void space is 32%  
(3) Electrical conductivity of semiconductors and metals increases with increase in temperature  
(4) Density of crystals decreases due to Schottky defect
14. Copper crystallises in fcc with a unit cell edge length of 361 pm. What is the radius of copper atom? [AIEEE-2011]  
(1) 181 pm (2) 128 pm (3) 157 pm (4) 108 pm
15. Lithium forms body centred cubic structure. The length of the side of its unit cell is 351 pm. Atomic radius of the lithium will be :- [Jee-Main (offline)-12]  
(1) 152 pm (2) 75 pm (3) 300 pm (4) 240 pm
16. In a face centred cubic lattice, atoms of A form the corner points and atoms of B form the face centred points. If two atoms of A are missing from the corner points, the formula of the ionic compound is [Jee-Main (online)-13]  
(1)  $AB_2$  (2)  $AB_3$  (3)  $AB_4$  (4)  $A_2B_5$
17. Which one of the following statements about packing in solids is **incorrect** ? [Jee-Main (online)-13]  
(1) Void space in ccp mode of packing is 26%  
(2) Coordination number in hcp mode of packing is 12  
(3) Void space in hcp mode of packing is 32%  
(4) Coordination number in bcc mode of packing is 8
18. An element having an atomic radius of 0.14 nm crystallizes in an fcc unit cell. What is the length of a side of the cell ? [Jee-Main (online)-13]  
(1) 0.96 nm (2) 0.4 nm (3) 0.24 nm (4) 0.56 nm

19. Experimentally it was found that a metal oxide has formula  $M_{0.98}O$ . Metal M, is present as  $M^{2+}$  and  $M^{3+}$  in its oxide. Fraction of the metal which exists as  $M^{3+}$  would be :- [Jee-Main (offline)-13]  
 (1) 7.01% (2) 4.08% (3) 6.05% (4) 5.08
20. The total number of octahedral void(s) per atom present in a cubic close packed structure is :- [Jee-Main (online)-14]  
 (1) 1 (2) 2 (3) 3 (4) 4
21. In a monoclinic unit cell, the relation of sides and angles are respectively [Jee-Main (online)-14]  
 (1)  $a \neq b \neq c$  and  $\alpha \neq \beta \neq \gamma \neq 90^\circ$  (2)  $a \neq b \neq c$  and  $\beta = \gamma = 90^\circ \neq \alpha$   
 (3)  $a = b \neq c$  and  $\alpha = \beta = \gamma = 90^\circ$  (4)  $a \neq b \neq c$  and  $\alpha = \beta = \gamma = 90^\circ$
22. The appearance of colour in solid alkali metal halides is generally due to : [Jee-Main (online)-14]  
 (1) Frenkel defect (2) F-centres (3) Schottky defect (4) Interstitial position
23. In a face centred cubic lattice atoms A are at the corner points and atoms B at the face centred points. If atom B is missing from one of the face centred points, the formula of the ionic compound is : [AIEEE-2011, Jee-Main (online)-14]  
 (1)  $AB_2$  (2)  $A_2B_3$  (3)  $A_5B_2$  (4)  $A_2B_5$
24. CsCl crystallises in body centred cubic lattice. if 'a' is its edge length then which of the following expression is correct : [Jee-Main (offline)-14]  
 (1)  $r_{Cs^+} + r_{Cl^-} = \frac{\sqrt{3}}{2}a$  (2)  $r_{Cs^+} + r_{Cl^-} = \sqrt{3}a$  (3)  $r_{Cs^+} + r_{Cl^-} = 3a$  (4)  $r_{Cs^+} + r_{Cl^-} = \frac{3a}{2}$
25. Sodium metal crystallizes in a body centred cubic lattice with a unit cell edge of  $4.29 \text{ \AA}$ . The radius of sodium atom is approximately :- [Jee-Main (offline)-15]  
 (1)  $5.72 \text{ \AA}$  (2)  $0.93 \text{ \AA}$  (3)  $1.86 \text{ \AA}$  (4)  $3.022 \text{ \AA}$
26. Which of the following compounds is metallic and ferromagnetic ? [Jee-Main (offline)-16]  
 (1)  $MnO_2$  (2)  $TiO_2$  (3)  $CrO_2$  (4)  $VO_2$
27. A metal crystallises in a face centred cubic structure. If the edge length of its unit cell is 'a', the closest approach between two atoms in metallic crystal will be :- [Jee-Main (offline)-17]  
 (1)  $2a$  (2)  $2\sqrt{2}a$  (3)  $\sqrt{2}a$  (4)  $\frac{a}{\sqrt{2}}$
28. Which type of effect 'defect' has the presence of cations in the interstitial sites - [Jee-Main (offline)-18]  
 (1) Vacancy defect (2) Frenkel defect  
 (3) Metal deficiency defect (4) Schottky defect
29. All of the following share the same crystal structure except :- [Jee-Main (online)-18]  
 (1) RbCl (2) CsCl (3) LiCl (4) NaCl
30. Which of the following arrangements shows the schematic alignment of magnetic moments of antiferromagnetic substance ? [Jee-Main (online)-18]  
 (1)  $\uparrow \downarrow \downarrow \downarrow \downarrow \uparrow$  (2)  $\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow$   
 (3)  $\uparrow \uparrow \downarrow \uparrow \uparrow \downarrow$  (4)  $\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$



## EXERCISE : J-ADVANCED

1. A metal crystallises into two cubic phases, FCC and BCC whose unit cell lengths are 3.5 and 3.0 Å respectively. Calculate the ratio of densities of FCC and BCC. [JEE-1999]
2. The coordination number of a metal crystallising in a hcp structure is [JEE-2000]  
(A) 12 (B) 4 (C) 8 (D) 6
3. In any ionic solid [MX] with schottky defects, the number of positive and negative ions are same. [T/F] [JEE-2000]
4. In a solid "AB" having NaCl structure "A" atoms occupy the corners of the cubic unit cell. If all the face-centred atoms along one of the axes are removed, then the resultant stoichiometry of the solid is  
(A)  $AB_2$  (B)  $A_2B$  (C)  $A_4B_3$  (D)  $A_3B_4$  [JEE-2000]
5. The figures given below show the location of atoms in three crystallographic planes in FCC lattice. Draw the unit cell for the corresponding structure and identify these planes in your diagram. [JEE-2000]



6. A substance  $A_xB_y$  crystallises in a FCC lattice in which atoms "A" occupy each corner of the cube and atoms "B" occupy the centres of each face of the cube. Identify the correct composition of the substance  $A_xB_y$ .  
(A)  $AB_3$  (B)  $A_4B_3$   
(C)  $A_3B$  (D) composition cannot be specified [JEE-2002]
7. Marbles of diameter 10 mm each are to be arranged on a flat surface so that their centres lie within the area enclosed by four lines of length each 40 mm. Sketch the arrangement that will give the maximum number of marbles per unit area, that can be enclosed in this manner and deduce the expression to calculate it. [JEE 2003]
8. (i) AB crystallizes in a rock salt structure with  $A : B = 1 : 1$ . The shortest distance between A and B is  $Y^{1/3}$  nm. The formula mass of AB is 6.023 Y amu where Y is any arbitrary constant. Find the density in  $kg\ m^{-3}$ .  
(ii) If measured density is  $20\ kg\ m^{-3}$ . Identify the type of point defect. [JEE-2004]
9. Which of the following FCC structure contains cations in alternate tetrahedral voids?  
(A) NaCl (B) ZnS (C)  $Na_2O$  (D)  $CaF_2$  [JEE 2005]
10. An element crystallises in FCC lattice having edge length 400 pm. Calculate the maximum diameter which can be placed in interstitial sites without disturbing the structure. [JEE 2005]

- 11.** The edge length of unit cell of a metal having atomic weight 75 g/mol is 5 Å which crystallizes in cubic lattice. If the density is 2 g/cc then find the radius of metal atom. ( $N_A = 6 \times 10^{23}$ ). Give the answer in pm.
- [JEE 2006]**

- 12.** Match the crystal system / unit cells mentioned in Column I with their characteristic features mentioned in Column II. Indicate your answer by darkening the appropriate bubbles of the  $4 \times 4$  matrix given in the ORS.

## Column I

- (A) simple cubic and face-centred cubic  
(B) cubic and rhombohedral  
(C) cubic and tetragonal  
(D) hexagonal and monoclinic

## Column II

- (P) have these cell parameters  $a = b = c$   
and  $\alpha = \beta = \gamma$   
(Q) are two crystal systems  
(R) have only two crystallographic angles of  $90^\circ$   
(S) belong to same crystal system.

**[JEE 2007]**

### Paragraph for Question No.13 to 15

In hexagonal systems of crystals, a frequently encountered arrangement of atoms is described as a hexagonal prism. Here, the top and bottom of the cell are regular hexagons and three atoms are sandwiched in between them. A space-filling model of this structure, called hexagonal close-packed (HCP), is constituted of a sphere on a flat surface surrounded in the same plane by six identical spheres as closely as possible. Three spheres are then placed over the first layer so that they touch each other and represent the second layer. Each one of these three spheres touches three spheres of the bottom layer. Finally, the second layer is covered with a third layer that is identical to the bottom layer in relative position. Assume radius of every sphere to be 'r'.

13. The number of atoms in this HCP unit cells is [JEE 2008]  
(A) 4 (B) 6 (C) 12 (D) 17

- 14.** The volume of this HCP unit cell is **[JEE 2008]**

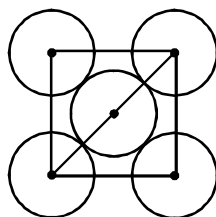
- (A)  $24\sqrt{2}r^3$       (B)  $16\sqrt{2}r^3$       (C)  $12\sqrt{2}r^3$       (D)  $\frac{64}{3\sqrt{3}}r^3$

15. The empty space in this HCP unit cell is [JEE 2008]  
(A) 74% (B) 47.6 % (C) 32% (D) 26%

16. The correct statement(s) regarding defects in solid is (are) [JEE 2009]

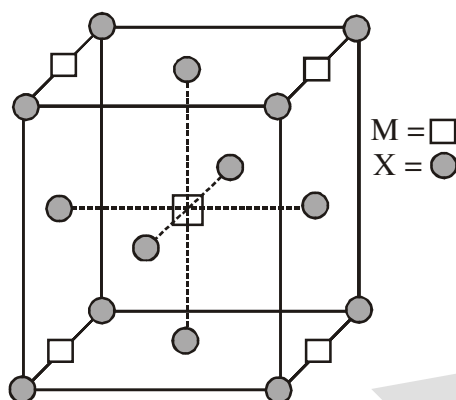
- (A) Frenkel defect is usually favoured by a very small difference in the sizes of cation and anion.
- (B) Frenkel defect is a dislocation defect
- (C) Trapping of an electron in the lattice leads to the formation of F-center.
- (D) Schottky defects have no effect on the physical properties of solids.

17. The packing efficiency of the two-dimensional square unit cell shown below is [JEE-2010]

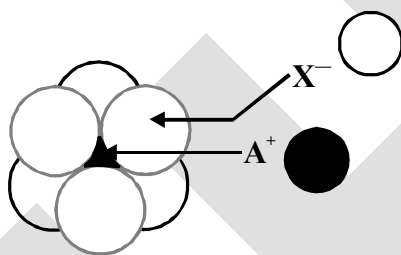


- (A) 39.27%                  (B) 68.02%                  (C) 74.05%                  (D) 78.54%

18. The number of hexagonal faces that present in a truncated octahedron is. [JEE-2011]
19. A compound  $M_pX_q$  has cubic close packing (ccp) arrangement of X. Its unit cell structure is shown below. The empirical formula of the compound is : [JEE-2012]



- (A) MX (B)  $MX_2$  (C)  $M_2X$  (D)  $M_5X_{14}$
20. The arrangement of  $X^-$  ions around  $A^+$  ion in solid AX is given in the figure (not drawn to scale). If the radius of  $X^-$  is 250 pm, the radius of  $A^+$  is - [JEE-2013]



- (A) 104 pm (B) 125 pm (C) 183 pm (D) 57 pm
21. If the unit cell of a mineral has cubic close packed (ccp) array of oxygen atoms with m fraction of octahedral holes occupied by aluminium ions and n fraction of tetrahedral holes occupied by magnesium ions m and n respectively, are - [JEE-2015]
- (A)  $\frac{1}{2}, \frac{1}{8}$  (B)  $1, \frac{1}{4}$  (C)  $\frac{1}{2}, \frac{1}{2}$  (D)  $\frac{1}{4}, \frac{1}{8}$
22. The **CORRECT** statement(s) for cubic close packed (ccp) three dimensional structure is (are)
- (A) The number of the nearest neighbours of an atom present in the topmost layer is 12
- (B) The efficiency of atom packing is 74% [JEE-2016]
- (C) The number of octahedral and tetrahedral voids per atom are 1 and 2, respectively
- (D) The unit cell edge length is  $2\sqrt{2}$  times the radius of the atom

23. A crystalline solid of a pure substance has a face-centred cubic structure with a cell edge of 400 pm. If the density of the substance in the crystal is  $8 \text{ g cm}^{-3}$ , then the number of atoms present in 256g of the crystal is  $N \times 10^{24}$ . The value of N is [JEE-2017]
24. Consider an ionic solid MX with NaCl structure. Construct a new structure (Z) whose unit cell is constructed from the unit cell of MX following the sequential instructions given below. Neglect the charge balance. [JEE-2018]

- (i) Remove all the anions (X) except the central one
- (ii) Replace all the face centered cations (M) by anions (X)
- (iii) Remove all the corner cations (M)
- (iv) Replace the central anion (X) with cation (M)

The value of  $\left( \frac{\text{number of anions}}{\text{number of cations}} \right)$  in Z is \_\_\_\_.

## ANSWER KEY

## S-I

- |                                                                   |                                   |
|-------------------------------------------------------------------|-----------------------------------|
| 1. Ans. (a) 300 pm, (b) 255 pm, (c) 210 pm                        | 2. Ans. 438 pm, 219 pm            |
| 3. Ans. 5.83 g cm <sup>-3</sup>                                   | 4. Ans. ( $\sqrt{2} : 1$ )        |
| 5. Ans. (0.9 gm/cm <sup>-3</sup> )                                | 6. Ans. A, B                      |
| 7. Ans. (64)                                                      | 8. Ans. (12)                      |
| 9. Ans. (6)                                                       | 10. Ans. (2)                      |
| 11. Ans. A <sub>2</sub> BC                                        | 12. Ans. (4)                      |
| 13. Ans. (0.293)                                                  | 14. Ans. ( $6 \times 10^{17}$ )   |
| 15. Ans. (2) $\frac{\frac{a}{\sqrt{2}} \times \sqrt{2}}{a/2} = 2$ | 16. Ans. (2.07 pm)                |
| 17. Ans. (6)                                                      | 18. Ans. (60%)                    |
| 19. Ans. 41.67 g cm <sup>-3</sup>                                 | 20. Ans. 0.60                     |
| 21. Ans. 4, 6, 8                                                  | 22. Ans. (6)                      |
| 23. Ans. ZnAl <sub>2</sub> O <sub>4</sub>                         | 24. Ans. 267 pm, 534 pm, 377.6 pm |
| 25. Ans. 346.4 pm                                                 | 26. Ans. 4                        |
| 27. Ans. a = 600 pm, V = $2.16 \times 10^{-22}$ cm <sup>3</sup>   | 28. Ans. 1.81 Å                   |
| 29. Ans. 4.34 Å                                                   | 30. Ans. (5 gm/cm <sup>3</sup> )  |
| 31. Ans. 15.05 %                                                  | 32. Ans. $6.0 \times 10^{18}$     |
| 33. Ans. 10                                                       | 34. Ans. 12.5%                    |
| 35. Ans. 3.0 gm/cm <sup>3</sup>                                   |                                   |

## S-II

- |                                                                                       |                            |
|---------------------------------------------------------------------------------------|----------------------------|
| 1. Ans. (2)                                                                           | 2. Ans. (5)                |
| 3. Ans. Ans. 8                                                                        | 4. Ans. 60%, +4            |
| 5. Ans. $5 \times 10^{24}$                                                            | 6. Ans. 0.72               |
| 7. Ans. 4                                                                             |                            |
| 8. Ans. (i) FCC (ii) 0.116 g/cc                                                       | 9. Ans. (a) 1.143, (b) 1.2 |
| 10. Ans. (a) MnF <sub>3</sub> , (b) 6, (c) 4.02 Å                                     |                            |
| 11. Ans. (a) 4.5 Å, (b) 5.2 Å, (c) 8, (d) 6, (e) 0.929 g/cm <sup>3</sup>              |                            |
| 12. Ans. 96%                                                                          | 13. Ans. (4)               |
| 14. Ans. Mg <sub>2</sub> SiO <sub>4</sub> , Fe <sub>2</sub> SiO <sub>4</sub> , 57.14% |                            |

*O-I*

- |             |             |             |
|-------------|-------------|-------------|
| 1. Ans.(A)  | 2. Ans.(D)  | 3. Ans.(A)  |
| 4. Ans.(D)  | 5. Ans.(C)  | 6. Ans.(C)  |
| 7. Ans. (C) | 8. Ans (B)  | 9. Ans (D)  |
| 10. Ans (B) | 11. Ans.(B) | 12. Ans.(C) |
| 13. Ans.(C) | 14. Ans.(C) | 15. Ans.(C) |
| 16. Ans.(A) | 17. Ans.(B) | 18. Ans (D) |
| 19. Ans (C) | 20. Ans (D) | 21. Ans.(C) |
| 22. Ans.(C) | 23. Ans.(C) | 24. Ans.(B) |
| 25. Ans.(A) | 26. Ans.(B) | 27. Ans.(A) |
| 28. Ans.(A) | 29. Ans.(D) | 30. Ans.(D) |
| 31. Ans.(D) | 32. Ans.(B) | 33. Ans(C)  |
| 34. Ans (C) | 35. Ans.(D) |             |

*O-II*

- |                                                                                                      |                  |                |
|------------------------------------------------------------------------------------------------------|------------------|----------------|
| 1. Ans. (C)                                                                                          | 2. Ans.(B)       | 3. Ans.(D)     |
| 4. Ans.(A,C)                                                                                         | 5. Ans.(B,C)     | 6. Ans.(A,C)   |
| 7. Ans.(A,B,D)                                                                                       | 8. Ans.(A,B,C,D) | 9. Ans.(A,B,D) |
| 10. Ans.(A,B,C,D)                                                                                    | 11. Ans.(B)      | 12. Ans.(D)    |
| 13. Ans.(C)                                                                                          | 14. Ans.(A)      | 15. Ans.(A)    |
| 16. Ans.(B)                                                                                          | 17. Ans.(D)      | 18. Ans.(C)    |
| 19. Ans.(B)                                                                                          | 20. Ans.(D)      | 21. Ans.(A)    |
| 22. Ans.(C)                                                                                          | 23. Ans.(A)      | 24. Ans.(D)    |
| 25. Ans.(A) $\rightarrow$ P, Q ; (B) $\rightarrow$ P,S ; (C) $\rightarrow$ P,R ; (D) $\rightarrow$ P |                  |                |
| 26. Ans.(A) $\rightarrow$ R,S ; (B) $\rightarrow$ P,Q,R,S ; (C) $\rightarrow$ Q                      |                  |                |
| 27. Ans.(A)                                                                                          | 28. Ans.(B)      |                |

*J-MAIN*

- |              |              |              |
|--------------|--------------|--------------|
| 1. Ans.(2)   | 2. Ans.(3)   | 3. Ans.(2)   |
| 4. Ans.(4)   | 5. Ans.(3)   | 6. Ans.(3)   |
| 7. Ans.(1)   | 8. Ans.(1)   | 9. Ans.(3)   |
| 10. Ans.(1)  | 11. Ans.(1)  | 12. Ans.(3)  |
| 13. Ans.(3)  | 14. Ans.(2)  | 15. Ans.(1)  |
| 16. Ans.(3)  | 17. Ans.(3)  | 18. Ans.(2)  |
| 19. Ans.(2)  | 20. Ans.(1)  | 21. Ans.(2)  |
| 22. Ans.(2)  | 23. Ans.(4)  | 24. Ans.(1)  |
| 25. Ans.(3)  | 26. Ans..(3) | 27. Ans. (4) |
| 28. Ans. (2) | 29. Ans. (2) | 30. Ans. (4) |

## J-ADVANCED

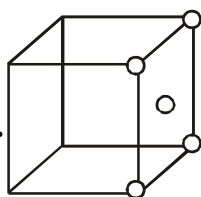
1. Ans.1.259

2. Ans.(A)

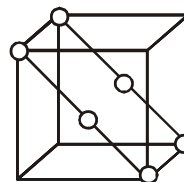
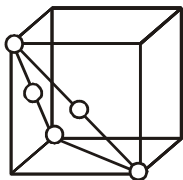
3. Ans.True

4. Ans.(D)

5. Ans.



fcc plan



6. Ans.(A)

7. Ans.18

8. Ans.(i) =  $5 \text{ kg m}^{-3}$ 

9. Ans.(B)

10. Ans. 117.1 pm

11. Ans. 216.5 pm

12. Ans. (A) P, S ; (B) -P,Q ; (C) - Q ; (D) - Q,R

13. Ans. (B)

14. Ans. (A)

15. Ans. (D)

16. Ans. (B,C)

17. Ans. (D)

18. Ans. (8)

19. Ans.(B)

20. Ans. (A)

21. Ans. (A)

22. Ans.(B,C,D)

23. Ans.(2)

24. Ans.(3)

## CHEMICAL EQUILIBRIUM

## KEY CONCEPTS

## TYPES OF REACTION:

- (i) Reversible (ii) Irreversible

## STATE OF EQUILIBRIUM

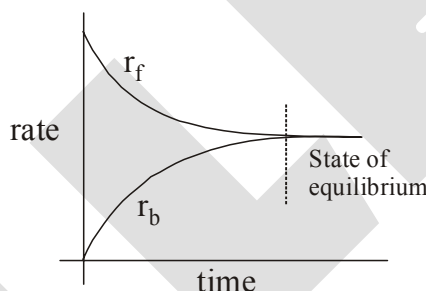
Most of the chemical reaction do not go to completion in a closed system and attain a state of equilibrium.

There are two approaches to understand nature of equilibrium. The One stems from thermodynamics. Equilibrium criteria is explained on the basis of thermodynamic function like  $\Delta H$  (change in enthalpy),  $\Delta S$  (change in entropy) and  $\Delta G$  (change in Gibb's function). At equilibrium macroscopic properties of the system like concentration, pressure ect. become constant at constant temperature.

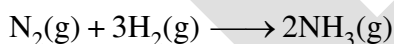
Other approach comes from kinetics as developed by Guldberg and Waage (1863). Equilibrium is said to have reached in a physical or chemical system when rate of forward and reverse processes are equal.

At equilibrium

**Rate of forward reaction = Rate of backward reaction.**



## Example:



Starting with pure  $\text{H}_2$  and  $\text{N}_2$  as reaction proceeds in forward direction. Ammonia is formed. At initially conc. of  $\text{H}_2$  and  $\text{N}_2$  drops and attain a steady value at equilibrium. On the others hand conc. of  $\text{NH}_3$  increases and at equilibrium attains a constant value.

Concentration time graphs for

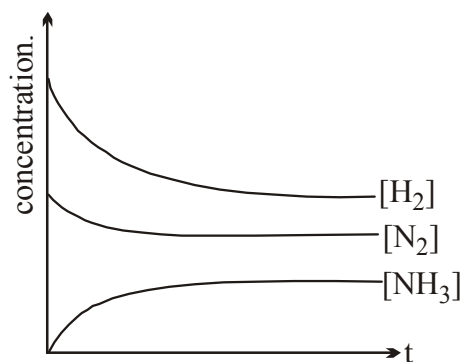


fig (1)

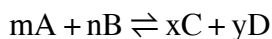


**IMPORTANT CHARACTERISTIC OF EQUILIBRIUM**

- (i) Equilibrium is possible only in closed system.
- (ii) The rate of forward process at equilibrium is equal to rate of backward process.
- (iii) All measurable properties of system remain constant over time. State of chemical equilibrium is characterised by equilibrium constant. Equilibrium constant have constant value at a given temperature.
- (iv) At equilibrium entropy of universe is maximized.
- (v) Both, *Kinetic* and *Thermodynamics* theories can be invoked to understand the extent to which a reaction proceed to forward direction. *e.g.* If extent of reaction is too large for forward direction (equilibrium is tilted heavily to forward direction) than
  - (a) Specific rate of forward reaction  $\gggg$  specific rate of backward reaction
  - (b) Gibb's function of product is vary small as compared to Gibb's function of reactant.

**LAW OF CHEMICAL EQUILIBRIUM OR MASS ACTION (By Guldberg and Waage)**

A general equation for a reversible reaction may be written



rate of reaction in inforward direction( $r_f$ )  $\propto [A]^m [B]^n$ ;  $r_f = k_f [A]^m [B]^n$

rate of reaction in inforward direction( $r_b$ )  $\propto [C]^x [D]^y$ ;  $r_b = k_b [C]^x [D]^y$

At equilibrium,  $r_f = r_b$

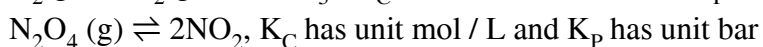
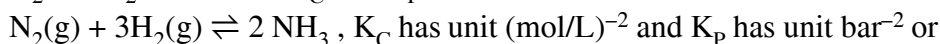
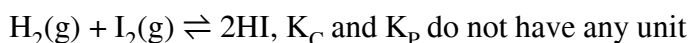
$$K_{eq} \text{ or } K_c = \frac{[C]^x [D]^y}{[A]^m [B]^n} \quad \text{where } K_c = k_f / k_b$$

where we use [ ] to indicate "molar concentration."

**Note :** We should calculate the value of  $K$  from the activities of the reactants and products rather than from their concentrations. However, the activity of a dilute solute is usefully approximated by its molar concentration, so we will use molar concentrations. However, for gases we can use molar concentrations of gases and partial pressure in our equilibrium calculations, The activity of a pure solid or pure liquid is constant, and the activity of a solvent in a dilute solution is also constant. Thus these species (solids, liquids, and solvents) are omitted from reactions quotients and equilibrium calculations.

**UNIT OF EQUILIBRIUM CONSTANT ( $K_C$ ,  $K_C^\circ$ ,  $K_P$  &  $K_P^\circ$ )**

We have already noted that the value of an equilibrium constant has meaning only when we give the corresponding balanced chemical equation. Its value changes for the new equation obtained by multiplying or dividing the original equation by a number. The value for equilibrium constant,  $K_C$  is calculate substituting the concentration in mol/L and for  $K_P$  by substituting partial pressure in Pa, kPa, etc. in atm. Thus, units of equilibrium constant will turn out to be units based on molarity or pressure, unless the sum of the exponents in the numerator is equal to the sum of the exponents in the denominator. Thus for the reaction:



However, these days we express equilibrium constants in dimensionless quantities by deviding concentration by 1 M and partial pressure by 1 bar.

\* **Relationship between  $K_P$  &  $K_C$** 

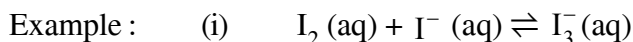
$$K_P = K_C (RT)^{\Delta ng}$$

### TYPE OF EQUILIBRIUM

(a) **Homogeneous chemical equilibria**

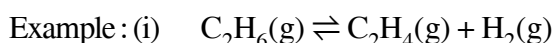
A homogeneous equilibrium is equilibrium with in a single phase i.e. when physical state of all the reactants and product are same.

(ii) **Liquid phase homogeneous equilibrium**



Eq. constants is  $K = \frac{[I_3^-(aq)]}{[I_2(aq)][I^-(aq)]}$

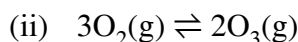
(iii) **Homogeneous equilibria in gases**



Eq. constants is

$$K_C = \frac{[C_2H_4][H_2]}{[C_2H_6]} \quad K_P = \frac{[P_{C_2H_4}][P_{H_2}]}{[P_{C_2H_6}]}$$

[ ] represents concentration in mol/litre at equilibrium  $P_{C_2H_4}$  & other are partial pressure at equilibrium



Eq. constants is

$$K_C = \frac{[O_3]^2}{[O_2]^3} \quad K_P = \frac{P_{O_3}^2}{P_{O_2}^3}$$

(b) **Heterogeneous equilibria**

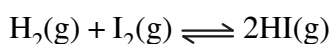
If reactants and product are found in two or more phases, the equilibria describing them is called heterogeneous equilibrium.



Eq. constants is  $K_P = \frac{1}{P_{CO_2}} \quad K_C = \frac{1}{[CO_2(g)]}$

### CHARACTERISTICS OF EQUILIBRIUM CONSTANT

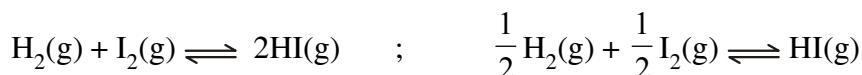
- The expression for equilibrium constant, K is applicable only when concentrations of the reactants and products have attained their equilibrium values and do not change with time.
- The value of equilibrium constant is independent of initial concentration of the reactants and product.
- Equilibrium constant has one unique value for a particular reaction represented by a balanced equation at a given temperature.
- The equilibrium constant for the reverse reaction is equal to the inverse of the equilibrium constant for the forward reaction.



$$K_P = \frac{P_{HI}^2}{P_{H_2} \cdot P_{I_2}} \quad ; \quad 2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

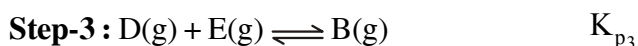
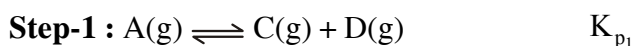
$$K_P' = \frac{1}{K_P}$$

- (v) The equilibrium constant  $K$ , for a reaction is related to the equilibrium constant of the corresponding reaction whose equation is obtained by multiplying or dividing the equation.



$$K_p'' = \frac{P_{\text{HI}}}{P_{\text{H}_2}^{1/2} \cdot P_{\text{I}_2}^{1/2}} = \sqrt{K_p}$$

- (vi) If reaction is performed in steps  
 $\text{A} \rightleftharpoons \text{B}$  ; overall reaction



### APPLICATION OF EQUILIBRIUM CONSTANT.

Now we will consider some applications of equilibrium constant and use it to answer question like:

- predicting the extent of a reaction on the basis of its magnitude.
- predicting the direction of the reaction, and
- calculating equilibrium concentration.

#### (i) Predicting the extent of a reaction

The magnitude of equilibrium constant is very useful especially in reactions of industrial importance. An equilibrium constant tells us whether we can expect a reaction mixture to contain a high or low concentration of product(s) at equilibrium. (It is important to note that an equilibrium constant tells us nothing about the rate at which equilibrium is reached). In the expression of  $K_C$  or  $K_p$ , product of the concentrations of products is written in numerator and the product of the concentrations of reactants is written in denominator. High value of equilibrium constant indicates that product(s) concentration is high and its low value indicates that concentration of the product(s) in equilibrium mixture is low.

For reaction,  $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightleftharpoons 2\text{HBr}(\text{g})$ , the value of

$$K_p = \frac{(P_{\text{HBr}})^2}{(P_{\text{H}_2})(P_{\text{Br}_2})} = 5.4 \times 10^{18}$$

The large value of equilibrium constant indicates that concentration of the product, HBr is very high and reaction goes nearly to completion.

Similarly, equilibrium constant for the reaction  $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{HCl}(\text{g})$  at 300 K is very high and reaction goes virtually to completion.

$$K_C = \frac{[\text{HCl}]^2}{[\text{H}_2][\text{Cl}_2]} = 4.0 \times 10^{31}$$

Thus, large value of  $K_p$  or  $K_C$  (larger than about  $10^3$ ), favour the products strongly. For intermediate values of  $K$  (approximately in the range of  $10^{-3}$  to  $10^3$ ), the concentrations of reactants and products are comparable. Small values of equilibrium constant (smaller than  $10^{-3}$ ), favour the reactants strongly.

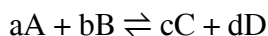
At 298 K for reaction,  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$

$$K_C = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = 4.8 \times 10^{-31}$$

The very small value of  $K_C$  implies that reactants  $\text{N}_2$  and  $\text{O}_2$  will be the predominant species in the reaction mixture at equilibrium.

(ii) **Predicting the direction of the reaction.**

The equilibrium constant is also used to find in which direction an arbitrary reaction mixture of reactants and products will proceed. For this purpose, we calculate the reaction quotient,  $Q$ . The reaction quotient is defined in the same way as the equilibrium constant (with molar concentrations to give  $Q_C$ , or with partial pressure to give  $Q_P$ ) at any stage of reaction. For a general reaction:



$$Q_C = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Then, if  $Q_C > K_C$ , the reaction will proceed in the direction of reactants (reverse reaction).

if  $Q_C < K_C$ , the reaction will move in the direction of the products

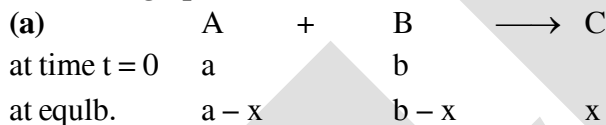
if  $Q_C = K_C$ , the reaction mixture is already at equilibrium.

In the reaction,  $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ , if the molar concentrations of  $H_2$ ,  $I_2$  and  $HI$  are  $0.1 \text{ mol L}^{-1}$  respectively at  $783 \text{ K}$ , then reaction quotient at this stage of the reaction is

$$Q_C = \frac{[HI]^2}{[H_2][I_2]} = \frac{(0.4)^2}{(0.1)(0.2)} = 8$$

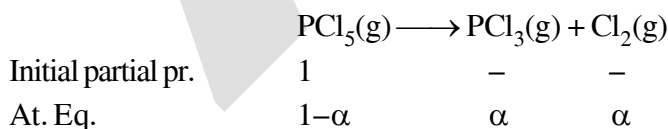
$K_C$  for this reaction at  $783 \text{ K}$  is 46 and we find that  $Q_C < K_C$ . The reaction, therefore, will move to right i.e. more  $H_2(g)$  and  $I_2(g)$  will react to form more  $HI(g)$  and their concentration will decrease till  $Q_C = K_C$ .

(iii) **Calculating equilibrium concentration.**



$$K_C = \frac{(x/V)}{\left(\frac{a-x}{V}\right)\left(\frac{b-x}{V}\right)} ; \quad K_P = \frac{\left(\frac{x}{a+b-x} P_T\right)}{\left(\frac{a-x}{a+b-x} P_T\right)\left(\frac{b-x}{a+b-x} P_T\right)}$$

(b) **Equilibrium constant expressions in term of ' $\alpha$ '**

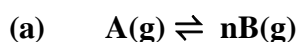


$$K_P = \frac{[p_{PCl_3(g)}][p_{Cl_2(g)}]}{p_{[PCl_5(g)]}} ; \quad K_C = \frac{\alpha^2}{1 - \alpha} \left( \frac{1}{V} \right)$$

$$K_P = \frac{\alpha \cdot \alpha}{1 - \alpha} \times \frac{P_T}{(1 + \alpha)}$$

$$K_P = \frac{\alpha^2}{1 - \alpha^2} P_T$$

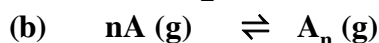
## (IV) Degree of dissociation in terms of molar mass and vapour density



$$\alpha = \frac{M_T - M_O}{M_O(n-1)} \quad \text{or} \quad \alpha = \frac{D_T - D_O}{D_O(n-1)}$$

 $M_T$  = Theoretical molar mass of reactant $M_O$  = Observed molar mass of mixture

$$D_T = \frac{M_T}{2} \quad \text{and} \quad D_O = \frac{M_O}{2}$$



|                          |               |                     |
|--------------------------|---------------|---------------------|
| Initial con <sup>n</sup> | a             | 0                   |
| at eq <sup>m</sup>       | $1(1-\alpha)$ | $\frac{a\alpha}{n}$ |

$$\alpha = \frac{M_T - M_O}{M_O\left(\frac{1}{n} - 1\right)}$$

**FACTOR'S AFFECTING EQUILIBRIA (Le-chatelier's principle)**(i) **Effect of change in concentration on equilibrium**

A chemical system at equilibrium can be shifted out of equilibrium by adding or removing one more of reactants or products. Shifting out of equilibrium doesn't mean that value of equilibrium constant change. Any alteration of concentration of reactant or product will disturb the equilibrium and concentration of reactant and product one readjust to one again attain equilibrium concentration.

In other word, as we add or remove reactant (or product) the ratio of equilibrium concentration become 'Q' (reaction quotient) and depending upon.

$Q < K$  : equilibrium will shift in forward direction.

$Q > K$  : equilibrium will shift in backward direction.

Example:  $Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons Fe(SCN)^{2+}(aq)$

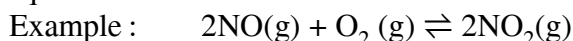
- (i) adding  $Fe^{3+}$  or  $SCN^-$  will more  $\frac{[Fe(SCN)^{2+}]}{[Fe^{3+}][SCN^-]} = Q$  less then  $K_C$  and equilibria will shift in forward direction.
- (ii) Removing  $Fe(SCN)^{2+}$  will have same effect
- (iii) Adding  $Fe(SCN)^{2+}$  from outside source in equilibrium mixture will have effect of increasing 'Q' hence reaction shift in backward direction.

(ii) **Effect of change in pressure**

Sometimes we can change the position of equilibrium by changing the pressure on a system. However, changes in pressure have a measurable effect only in system where gases are involved – and then only when the chemical reaction produces a change in the total number of gas molecules in the system.

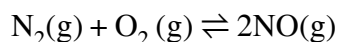
As we increase the pressure of a gaseous system at equilibrium, either by decreasing the volume of the system or by adding more of the equilibrium mixture, we introduce a stress by increasing the number of molecules per unit of volume. In accordance with Le Chatelier's principle, a chemical reaction that reduces the total number of molecules per unit of volume will be favored because this relieves the stress. The reverse reaction would be favoured by a decrease in pressure.

Consider what happens when we increase the pressure on a system in which NO, O<sub>2</sub> and NO<sub>2</sub> are in equilibrium.



The formation of additional amounts of NO<sub>2</sub> decreases the total number of molecules in the system, because each time two molecules of NO<sub>2</sub> form, a total of three molecules of NO and O<sub>2</sub> react. This reduces the total pressure exerted by the system and reduces, but does not completely relieve, the stress of the increased pressure. On the other hand, a decrease in the pressure on the system favors decomposition of NO<sub>2</sub> into NO and O<sub>2</sub> which tends to restore the pressure.

Let us now consider the reaction



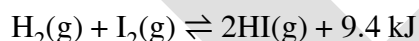
Because there is no change in the total number of molecules in the system during reaction, a change in pressure does not favor either formation or decomposition of gaseous nitric oxide.

### (iii) Effect of change in temperature on equilibrium

Changing concentration or pressure upsets an equilibrium because the reaction quotient is shifted away from the equilibrium value. Changing the temperature of a system at equilibrium has a different effect: A change in temperature changes the value of the equilibrium constant. However, we can predict the effect of the temperature change by treating it as a stress on the system and applying Le Chatelier's principle. When hydrogen reacts with gaseous iodine, energy is released as heat is evolved.



Because this reaction is exothermic, we can write it with heat as a product.



Increasing the temperature of the reaction increases the amount of energy present. Thus, increasing the temperature has the effect of increasing the amount of one of the products of this reaction. The reaction shifts to the left to relieve the stress, and there is an increase in the concentration of H<sub>2</sub> and I<sub>2</sub> and a reduction in the concentration of HI. When we change the temperature of a system at equilibrium, the equilibrium constant for the reaction changes. Lowering the temperature in the HI system increases the equilibrium constant from 50.0 at 400°C to 67.5 at 357°C. At equilibrium at the lower temperature, the concentration of HI has increased and the concentrations of H<sub>2</sub> and I<sub>2</sub> have decreased. Raising the temperature decreases the value of the equilibrium constant from 67.5 at 357°C to 50.0 at 400°C.

### van't Hoff equation

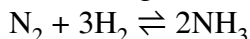
$$(a) \quad \frac{d(\ln K)}{dT} = \frac{\Delta H^\circ}{RT^2}$$

$$\ln \left( \frac{K_2}{K_1} \right) = - \frac{\Delta H^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

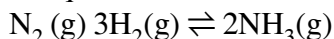
(iv) *Effect of catalyst on equilibrium*

A catalyst has no effect on the value of an equilibrium constant or on equilibrium concentrations. The catalyst merely increase the rates of both the forward and the reverse reactions to the same extent so that equilibrium is reached more rapidly.

All of these effects change in concentration or pressure, change in temperature, and the effect of a catalyst on a chemical equilibrium play a role in the industrial synthesis of ammonia from nitrogen and hydrogen according to the equation.

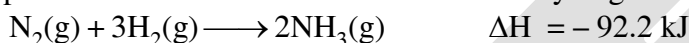


One way to increase the yield of ammonia is to increase the pressure on the system in which  $\text{N}_2$ ,  $\text{H}_2$  and  $\text{NH}_3$  are in equilibrium or are coming to equilibrium.



The formation of additional amounts of ammonia reduces the total pressure exerted by the system and somewhat reduces the stress of the increased pressure.

Although increasing the pressure of a mixture of  $\text{N}_2$ ,  $\text{H}_2$  and  $\text{NH}_3$  increase the yield ammonia, at low temperatures the rate of formation of ammonia is slow. At room temperature, for example, the reaction is so slow that if we prepared a mixture of  $\text{N}_2$  and  $\text{H}_2$ , no detectable amount of ammonia would form during our lifetime. Attempts to increase the rate of the reaction by increasing the temperature are counterproductive. The formation of ammonia from hydrogen and nitrogen is an exothermic process:



Thus increasing the temperature to increase the rate lowers the yield. If we lower the temperature to shift the equilibrium to the right to favour the formation of more ammonia, equilibrium is reached more slowly because of the large decrease of reaction rate with decreasing temperature.

Part of the rate of formation lost by operating at lower temperatures can be recovered by using a catalyst to increase the reaction rate. Iron powder is one catalyst used. However, as we have seen, a catalyst serves equally well to increase the rate of a reverse reaction in this case, the decomposition of ammonia into its constituent elements. Thus the net effect of the iron catalyst on the reaction is to cause equilibrium to be reached more rapidly.

**A THERMODYNAMIC RELATIONSHIP :**

$$\Delta G = \Delta G^\circ + RT \ln Q \quad [Q = \text{Reaction quotient}]$$

$$\Delta G^\circ = -RT \ln K_{\text{eq}} \quad (\text{At eq}^m, (\Delta G)_{T,P} = 0)$$

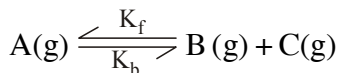
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\ln K_{\text{eq}} = \frac{-\Delta_r H^\circ}{RT} + \frac{\Delta_r S^\circ}{R}$$

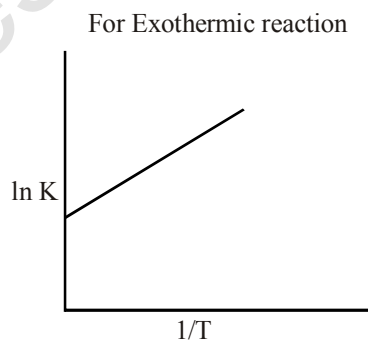
$$\ln K_1 = \frac{\Delta_r S^\circ}{R} - \frac{\Delta_r H^\circ}{RT_1}$$

$$\ln K_2 = \frac{\Delta_r S^\circ}{R} - \frac{\Delta_r H^\circ}{RT_2}$$

$$\ln \left( \frac{K_2}{K_1} \right) = \frac{\Delta H^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

**EQUILIBRIUM CONSTANT AS PER KINETICS :**

$$\frac{-d(\text{A})}{dt} = K_f [\text{A}] - K_b [\text{B}] [\text{C}]$$



$$\text{At eq}^m \quad \frac{-d[A]}{dt} = 0 \quad \frac{K_f}{K_b} = \frac{[B][C]}{[A]} = K_c$$

where  $k = A \cdot e^{-E_a/RT}$  ;  $A$  : pre-exponential factor

$$k_f = A_f \cdot e^{-E_{a(f)}/RT}$$

$E_a$  : activation energy

$$k_b = A_b \cdot e^{-E_{a(b)}/RT}$$

$$K_{eq} = \frac{k_f}{k_b} = \frac{A_f \cdot e^{-E_{a(f)}/RT}}{A_b \cdot e^{-E_{a(b)}/RT}}$$

$$k = A \cdot e^{-\Delta H/RT}$$

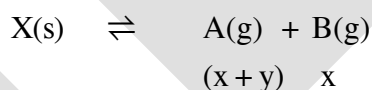
where  $\Delta H = E_{a(f)} - E_{a(b)}$

$$\ln K_1 = \ln A - \frac{\Delta H}{RT_1}$$

$$\ln K_2 = \ln A - \frac{\Delta H}{RT_2}$$

$$\ln \frac{K_2}{K_1} = \frac{\Delta H}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

### SIMULTANEOUS EQUILIBRIA :



$$K_{P_1} = (x+y)x$$



$$K_{P_2} = (x+y)y$$

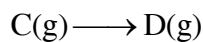
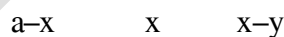
$$\frac{K_{P_1}}{K_{P_2}} = \frac{x}{y}$$

$$P_{total} = 2x + 2y$$

### SEQUENTIAL EQUILIBRIUM :



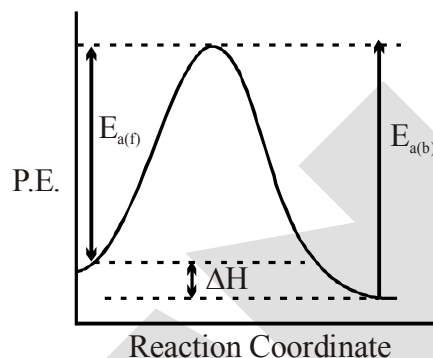
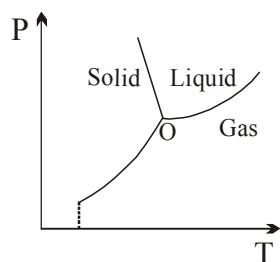
$$K_{C_1} = (x)(x-y)$$



$$K_{C_2} = \frac{y}{x-y}$$



### PHASE DIAGRAM FOR WATER:





## EXERCISE # O-I

Only one is correct

- $x \rightleftharpoons y$  reaction is said to be in equilibrium, when :-

(A) Only 10% conversion of x to y takes place  
 (B) Complete conversion of x to y has taken place  
 (C) Conversion of x to y is only 50% complete  
 (D) The rate of change of x to y is just equal to the rate of change of y to x in the system
- The equilibrium concentration of B  $[(B)_e]$  for the reversible reaction  $A \rightleftharpoons B$  can be evaluated by the expression:-

(A)  $K_c [A]_e^{-1}$       (B)  $\frac{k_f}{k_b} [A]_e^{-1}$       (C)  $k_f k_b^{-1} [A]_e$       (D)  $k_f k_b [A]^{-1}$
- In a chemical equilibrium, the rate constant for the backward reaction is  $2 \times 10^{-4}$  and the equilibrium constant is 1.5. The rate constant for the forward reaction is:-

(A)  $2 \times 10^{-3}$       (B)  $5 \times 10^{-4}$       (C)  $3 \times 10^{-4}$       (D)  $9.0 \times 10^{-4}$
- For which reaction is  $K_p = K_c$  :-

(A)  $2\text{NOCl(g)} \rightleftharpoons 2\text{NO(g)} + \text{Cl}_2\text{(g)}$       (B)  $\text{N}_2\text{(g)} + 3\text{H}_2\text{(g)} \rightleftharpoons 2\text{NH}_3\text{(g)}$   
 (C)  $\text{H}_2\text{(g)} + \text{I}_2\text{(g)} \rightleftharpoons 2\text{HI(g)}$       (D)  $2\text{SO}_2\text{(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2\text{SO}_3\text{(g)}$
- For the reaction  
 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}_{(s)} \rightleftharpoons \text{CuSO}_4 \cdot 3\text{H}_2\text{O}_{(s)} + 2\text{H}_2\text{O}_{(g)}$   
 Which one is correct representation :-

(A)  $K_p = (P_{\text{H}_2\text{O}})^2$       (B)  $K_c = [\text{H}_2\text{O}]^2$       (C)  $K_p = K_c (RT)^2$       (D) All
- $\log \frac{K_p}{K_c} + \log RT = 0$  is true relationship for the following reaction:-

(A)  $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$       (B)  $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$   
 (C)  $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$       (D) (B) and (C) both
- For a reaction  $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ , the value of  $K_c$  does not depends upon :-

(a) Initial concentration of the reactants      (b) Pressure  
 (c) Temperature      (d) Catalyst  
 (A) Only c      (B) a, b, c      (C) a, b, d      (D) a, b, c, d
- For any reversible reaction if concentration of reactants increases then effect on equilibrium constant:-

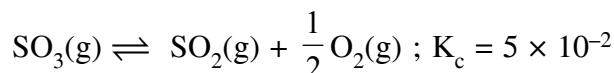
(A) Depends on amount of concentration      (B) Unchange  
 (C) Decrease      (D) Increase
- If some He gas is introduced into the equilibrium  $\text{PCl}_{5(g)} \rightleftharpoons \text{PCl}_{3(g)} + \text{Cl}_{2(g)}$  at constant pressure and temperature then equilibrium constant of reaction:

(A) Increase      (B) Decrease      (C) Unchange      (D) Nothing can be said

10. The equilibrium constant for the reaction ;  
 $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$  at temperature  
 T is  $4 \times 10^{-4}$ . The value of  $K_c$  for the reaction.

$\text{NO}(\text{g}) \rightleftharpoons \frac{1}{2} \text{N}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g})$  at the same temperature is :

- (A) 0.02 (B) 50 (C)  $4 \times 10^{-4}$  (D)  $2.5 \times 10^{-2}$
11. The equilibrium constant for the given reaction :



The value of  $K_c$  for the reaction :

$2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$ , will be

- (A) 400 (B)  $2.40 \times 10^{-3}$  (C)  $9.8 \times 10^{-2}$  (D)  $4.9 \times 10^{-2}$
12. For the following three reactions 1, 2 and 3, equilibrium constants are given :
- (1)  $\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{H}_2(\text{g}) ; K_1$   
 (2)  $\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + 3\text{H}_2(\text{g}) ; K_2$   
 (3)  $\text{CH}_4(\text{g}) + 2\text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + 4\text{H}_2(\text{g}) ; K_3$
- Which of the following relations is correct ?

- (A)  $K_1 \sqrt{K_2} = K_3$  (B)  $K_2 K_3 = K_1$  (C)  $K_3 = K_1 K_2$  (D)  $K_3 \cdot K_2^3 K_1^2$

13. Sulfide ion in alkaline solution reacts with solid sulfur to form polysulfide ions having formulas  $\text{S}_2^{2-}$ ,  $\text{S}_3^{2-}$ ,  $\text{S}_4^{2-}$  and so on. The equilibrium constant for the formation of  $\text{S}_2^{2-}$  is 12 ( $K_1$ ) & for the formation of  $\text{S}_3^{2-}$  is 132 ( $K_2$ ), both from S and  $\text{S}^{2-}$ . What is the equilibrium constant for the formation of  $\text{S}_3^{2-}$  from  $\text{S}_2^{2-}$  and S?

- (A) 11 (B) 12 (C) 132 (D) None of these

14. What should be the value of  $K_c$  for the reaction  $2\text{SO}_{2(\text{g})} + \text{O}_{2(\text{g})} \rightleftharpoons 2\text{SO}_{3(\text{g})}$ , if the amount are  $\text{SO}_3 = 48 \text{ g}$ ,  $\text{SO}_2 = 12.8 \text{ g}$  and  $\text{O}_2 = 9.6 \text{ g}$  at equilibrium and the volume of the container is one litre?

- (A) 64 (B) 30 (C) 42 (D) 8.5

15. In the reaction,  $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$ , the amount of each  $\text{PCl}_5$ ,  $\text{PCl}_3$  and  $\text{Cl}_2$  is 2 mole at equilibrium and total pressure is 3 atmosphere. The value of  $K_p$  will be

- (A) 1.0 atm. (B) 3.0 atm. (C) 2.9 atm. (D) 6.0 atm.

16. For the reaction :  $\text{P} \rightleftharpoons \text{Q} + \text{R}$ . Initially 2 moles of P was taken. Up to equilibrium 0.5 moles of P was dissociated. What would be the degree of dissociation :-

- (A) 0.5 (B) 1 (C) 0.25 (D) 4.2

17. 4 moles of  $\text{PCl}_5$  are heated at constant temperature in closed container. If degree of dissociation for  $\text{PCl}_5$  is 0.5 calculate total number of moles at equilibrium :-

- (A) 4.5 (B) 6 (C) 3 (D) 4

18. In the reaction  $2P(g) + Q(g) \rightleftharpoons 3R(g) + S(g)$ . If 2 moles each of P and Q taken initially in a 1 litre flask. At equilibrium which is true:-  
 (A)  $[P] < [Q]$  (B)  $[P] = [Q]$  (C)  $[Q] = [R]$  (D) None of these
19. For the reaction  $A + 2B \rightleftharpoons 2C + D$ , initial concentration of A is  $a$  and that of B is 1.5 times that of A. Concentration of A and D are same at equilibrium. What should be the concentration of B at equilibrium ?  
 (A)  $\frac{a}{4}$  (B)  $\frac{a}{2}$  (C)  $\frac{3a}{4}$  (D) All of the above.
20. For the reaction  $3A(g) + B(g) \rightleftharpoons 2C(g)$  at a given temperature,  $K_c = 9.0$ . What must be the volume of the flask, if a mixture of 2.0 mol each of A, B and C exist in equilibrium?  
 (A) 6L (B) 9L (C) 36 L (D) None of these
21. For the following gases equilibrium.  $N_2O_4(g) \rightleftharpoons 2NO_2(g)$   
 $K_p$  is found to be equal to  $K_c$ . This is attained when temperature is  
 (A)  $0^\circ\text{C}$  (B) 273 K (C) 1 K (D) 12.19 K
22. The degree of dissociation of  $SO_3$  is  $\alpha$  at equilibrium pressure  $p^0$ .  
 $K_p$  for  $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$   
 (A)  $\frac{p^0 \alpha^3}{2(1-\alpha)^3}$  (B)  $\frac{p^0 \alpha^3}{(2+\alpha)(1-\alpha)^2}$  (C)  $\frac{p^0 \alpha^2}{2(1-\alpha)^2}$  (D) None of these
23. For the reaction :  $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$ , the degree of dissociated ( $\alpha$ ) of  $HI(g)$  is related to equilibrium constant  $K_p$  by the expression  
 (A)  $\frac{1+2\sqrt{K_p}}{2}$  (B)  $\sqrt{\frac{1+2K_p}{2}}$  (C)  $\sqrt{\frac{2K_p}{1+2K_p}}$  (D)  $\frac{2\sqrt{K_p}}{1+2\sqrt{K_p}}$
24. The equilibrium constant for the reaction  
 $A(g) + 2B(g) \rightleftharpoons C(g)$   
 is  $0.25 \text{ dm}^6 \text{ mol}^{-2}$ . In a volume of  $5 \text{ dm}^3$ , what amount of A must be mixed with 4 mol of B to yield 1 mol of C at equilibrium.  
 (A) 3 moles (B) 24 moles (C) 26 moles (D) None of these
25. The equilibrium constant  $K_c$  for the reaction,  
 $A(g) + 2B(g) \rightleftharpoons 3C(g)$  is  $2 \times 10^{-3}$   
 What would be the equilibrium partial pressure of gas C if initial pressure of gas A & B are 1 & 2 atm respectively.  
 (A) 0.0625 atm (B) 0.1875 atm (C) 0.21 atm (D) None of these
26. A 20.0 litre vessel initially contains 0.50 mole each of  $H_2$  and  $I_2$  gases. These substances react and finally reach an equilibrium condition. Calculate the equilibrium concentration of HI if  $K_{eq} = 49$  for the reaction  $H_2 + I_2 \rightleftharpoons 2HI$ .  
 (A) 0.78 M (B) 0.039 M (C) 0.033 M (D) 0.021 M

27. At 675 K,  $\text{H}_2(\text{g})$  and  $\text{CO}_2(\text{g})$  react to form  $\text{CO}(\text{g})$  and  $\text{H}_2\text{O}(\text{g})$ ,  $K_p$  for the reaction is 0.16. If a mixture of 0.25 mole of  $\text{H}_2(\text{g})$  and 0.25 mol of  $\text{CO}_2$  is heated at 675 K, mole % of  $\text{CO}(\text{g})$  in equilibrium mixture is :
- (A) 7.14 (B) 14.28 (C) 28.57 (D) 33.33
28. The vapour density of  $\text{N}_2\text{O}_4$  at a certain temperature is 30. What is the % dissociation of  $\text{N}_2\text{O}_4$  at this temperature?
- (A) 53.3% (B) 106.6% (C) 26.7% (D) None
29. The equilibrium constant  $K_p$  (in atm) for the reaction is 9 at 7 atm and 300 K.
- $$\text{A}_2(\text{g}) \rightleftharpoons \text{B}_2(\text{g}) + \text{C}_2(\text{g})$$
- Calculate the average molar mass (in gm/mol) of an equilibrium mixture.
- Given :** Molar mass of  $\text{A}_2$ ,  $\text{B}_2$  and  $\text{C}_2$  are 70, 49 & 21 gm/mol respectively.
- (A) 50 (B) 45 (C) 40 (D) 37.5
30. Vapour density of the equilibrium mixture of the reaction
- $$2\text{NH}_3(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$$
- is 6.0
- Percent dissociation of ammonia gas is:
- (A) 13.88 (B) 58.82 (C) 41.66 (D) None of these
31. The equilibrium  $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$  shifts forward if :-
- (A) A catalyst is used.  
(B) An adsorbent is used to remove  $\text{SO}_3$  as soon as it is formed.  
(C) Small amounts of reactants are removed.  
(D) None of these
32. In manufacture of NO, the reaction  $\text{N}_{2(\text{g})} + \text{O}_{2(\text{g})} \rightleftharpoons 2\text{NO}_{(\text{g})}$ ,  $\Delta H$  +ve is favourable if :-
- (A) Pressure is increased (B) Pressure is decreased  
(C) Temperature is increased (D) Temperature is decreased
33. For the reaction  $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$ , the degree of dissociation varies inversely as the square root of pressure of the system. Supposing at constant temperature If the volume is increased 16 times the initial volume, the degree of dissociation for this reaction will become :-
- (A) 4 times (B)  $\frac{1}{4}$  times (C) 2 times (D)  $\frac{1}{2}$  times
34. In which of the following reactions, increase in the pressure at constant temperature does not affect the moles at equilibrium :
- (A)  $2\text{NH}_3(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$  (B)  $\text{C}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{CO}(\text{g})$   
(C)  $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g})$  (D)  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$
35. Change in volume of the system does not alter the number of moles in which of the following equilibrium
- (A)  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$  (B)  $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$   
(C)  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$  (D)  $\text{SO}_2\text{Cl}_2(\text{g}) \rightleftharpoons \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$

36. The conditions favourable for the reaction :



are :

- (A) low temperature, high pressure (B) any value of T and P  
(C) low temperature and low pressure (D) high temperature and high pressure
37. Densities of diamond and graphite are 3.5 and 2.3 gm/mL.



favourable conditions for formation of diamond are

- (A) high pressure and low temperature (B) low pressure and high temperature  
(C) high pressure and high temperature (D) low pressure and low temperature
38. The equilibrium  $\text{SO}_2\text{Cl}_2(\text{g}) \rightleftharpoons \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$  is attained at  $25^\circ\text{C}$  in a closed rigid container and an inert gas, helium is introduced. Which of the following statements is/are correct.
- (A) concentrations of  $\text{SO}_2$ ,  $\text{Cl}_2$  and  $\text{SO}_2\text{Cl}_2$  do not change  
(B) more chlorine is formed  
(C) concentration of  $\text{SO}_2$  is reduced  
(D) more  $\text{SO}_2\text{Cl}_2$  is formed
39. The yield of product in the reaction



would be lower at :

- (A) low temperature and low pressure (B) high temperature & high pressure  
(C) low temperature and to high pressure (D) high temperature & low pressure
40. What is the effect of the reduction of the volume of the system for the equilibrium  $2\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{CO}(\text{g})$  ?
- (A) The equilibrium will be shifted to the left by the increased pressure caused by the reduction in volume.  
(B) The equilibrium will be shifted to the right by the decreased pressure caused by the reduction in volume.  
(C) The equilibrium will be shifted to the left by the increased pressure caused by the increase in volume.  
(D) The equilibrium will be shifted to the right by the increased pressure caused by the reduction in volume.

## J-MAIN

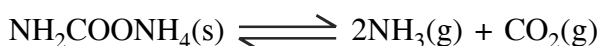
1. The equilibrium constants at 298 K for a reaction  $A + B \rightleftharpoons C + D$  is 100. If the initial concentration of all the four species were 1 M each, then equilibrium concentration of D (in mol L<sup>-1</sup>) will be :  
[JEE-MAINS-16]

(1) 1.182                      (2) 0.182                      (3) 0.818                      (4) 1.818

2. For the reaction  $SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)}$ , if  $K_p = K_C (RT)^x$  where the symbols have usual meaning then the value of x is : (assuming ideality)  
[JEE-MAINS-14]

(1)  $\frac{1}{2}$                       (2) 1                      (3) -1                      (4)  $-\frac{1}{2}$

3. For the decomposition of the compound, represented as  
[JEE-MAINS(online)-14]



the  $K_p = 2.9 \times 10^{-5} \text{ atm}^3$ .

If the reaction is started with 1 mol of the compound, the total pressure at equilibrium would be

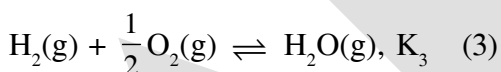
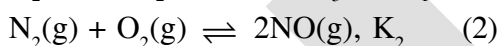
(1)  $38.8 \times 10^{-2} \text{ atm}$                       (2)  $1.94 \times 10^{-2} \text{ atm}$   
(3)  $5.82 \times 10^{-2} \text{ atm}$                       (4)  $7.66 \times 10^{-2} \text{ atm}$

4. In reaction  $A + 2B \rightleftharpoons 2C + D$ , initial concentration of B was 1.5 times of [A], but at equilibrium the concentrations of A and B became equal. The equilibrium constant for the reaction is :

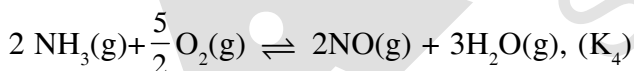
[JEE-MAINS(online)-13]

(1) 4                      (2) 6                      (3) 12                      (4) 8

5.  $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ ,  $K_1$  (1)  
[JEE-MAINS(online)-13]



The equation for the equilibrium constant of the reaction



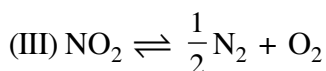
in terms of  $K_1$ ,  $K_2$  and  $K_3$  is :

(1)  $\frac{K_1 K_3^2}{K_2}$                       (2)  $\frac{K_2 K_3^3}{K_1}$                       (3)  $\frac{K_1 K_2}{K_3}$                       (4)  $K_1 K_2 K_3$

6. One mole of  $O_2(g)$  and two moles of  $SO_2(g)$  were heated in a closed vessel of one litre capacity at 1098 K. At equilibrium 1.6 moles of  $SO_3(g)$  were found. The equilibrium constant  $K_C$  of the reaction would be :-  
[JEE-MAINS(online)-12]

(1) 60                      (2) 80                      (3) 30                      (4) 40

7.  $K_1$ ,  $K_2$  and  $K_3$  are the equilibrium constants of the following reactions (I), (II) and (III), respectively  
 (I)  $N_2 + 2O_2 \rightleftharpoons 2NO_2$  (II)  $2NO_2 \rightleftharpoons N_2 + 2O_2$  [JEE-MAINS(online)-12]



The correct relation from the following is :

(1)  $K_1 = \sqrt{K_2} = K_3$  (2)  $K_1 = \frac{1}{K_2} = \frac{1}{K_3}$  (3)  $K_1 = \frac{1}{K_2} = K_3$  (4)  $K_1 = \frac{1}{K_2} = \frac{1}{(K_3)^2}$

8. The value of  $K_p$  for the equilibrium reaction  $N_2O_4(g) \rightleftharpoons 2NO_2(g)$  is 2. The percentage dissociation of  $N_2O_4(g)$  at a pressure of 0.5 atm is [JEE-MAINS(online)-12]

(1) 71 (2) 50 (3) 88 (4) 25

9. 8 mol of  $AB_3(g)$  are introduced into a 1.0 dm<sup>3</sup> vessel. If it dissociates as  $2AB_3(g) \rightleftharpoons A_2(g) + 3B_2(g)$  At equilibrium, 2mol of  $A_2$  are found to be present. The equilibrium constant of this reaction is :- [JEE-MAINS(online)-12]

(1) 36 (2) 3 (3) 27 (4) 2

10. The equilibrium constant ( $K_C$ ) for the reaction  $N_2(g) + O_2(g) \longrightarrow 2NO(g)$  at temperature T is  $4 \times 10^{-4}$ . The value of  $K_C$  for the reaction.  $NO(g) \longrightarrow \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g)$  at the same temperature is :- [AIEEE-2012]

(1) 50.0 (2) 0.02 (3)  $2.5 \times 10^2$  (4)  $4 \times 10^{-4}$

11. A vessel at 1000 K contains  $CO_2$  with a pressure of 0.5 atm. Some of the  $CO_2$  is converted into CO on the addition of graphite. If the total pressure at equilibrium is 0.8 atm, the value of K is :- [AIEEE-2011]

(1) 0.3 atm (2) 0.18 atm (3) 1.8 atm (4) 3 atm

12. The equilibrium constants  $K_{p1}$  and  $K_{p2}$  for the reaction  $X \rightleftharpoons 2Y$  and  $Z \rightleftharpoons P + Q$ , respectively are in the ratio of 1 : 9. If the degree of dissociation of X and Z be equal then the ratio of total pressure at these equilibria is [AIEEE-2008]

(1) 1 : 36 (2) 1 : 1 (3) 1 : 3 (4) 1 : 9

13. Phosphorus pentachloride dissociates as follows, in a closed reaction vessel, [AIEEE-2006]



If total pressure at equilibrium of the reaction mixture is P and degree of dissociation of  $PCl_5$  is x, the partial pressure of  $PCl_3$  will be-

(1)  $\left(\frac{2x}{1-x}\right)P$  (2)  $\left(\frac{x}{x-1}\right)P$  (3)  $\left(\frac{x}{1-x}\right)P$  (4)  $\left(\frac{x}{x+1}\right)P$

14. The equilibrium constant for the reaction  $SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2(g)$  is  $K_C = 4.9 \times 10^{-2}$ . The value of  $K_C$  for the reaction [AIEEE-2006]



(1)  $2.40 \times 10^{-3}$  (2)  $9.8 \times 10^{-2}$  (3)  $4.9 \times 10^{-2}$  (4) 416

15. For the reaction  $2\text{NO}_{2(g)} \rightleftharpoons 2\text{NO}_{(g)} + \text{O}_{2(g)}$ , ( $K_c = 1.8 \times 10^{-6}$  at  $184^\circ\text{C}$ ) ( $R = 0.831 \text{ kJ}(\text{mol.K})$ )  
When  $K_p$  and  $K_c$  are compared at  $184^\circ\text{C}$  it is found that [AIEEE-2005]

- (1)  $K_p$  is less than  $K_c$
- (2)  $K_p$  is greater than  $K_c$
- (3) Whether  $K_p$  is greater than, less than or equal to  $K_c$  depends upon the total gas pressure
- (4)  $K_p = K_c$

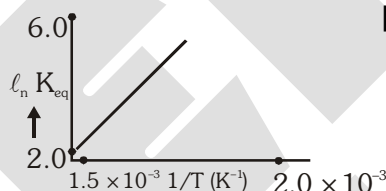
16. The exothermic formation of  $\text{ClF}_3$  is represented by the equation [AIEEE-2005]



Which of the following will increase the quantity of  $\text{ClF}_3$  in an equilibrium mixture of  $\text{Cl}_2$ ,  $\text{F}_2$  and  $\text{ClF}_3$ ?

- (1) Removing  $\text{Cl}_2$
- (2) Increasing the temperature
- (3) Adding  $\text{F}_2$
- (4) Increasing the volume of the container

17. A schematic plot of  $\ln K_{eq}$  versus inverse of temperature for a reaction is shown below. The reaction must be [AIEEE-2005]



- (1) endothermic
- (2) exothermic
- (3) highly spontaneous at ordinary temperature
- (4) one with negligible enthalpy change

18. What is the equilibrium expression for the reaction  $\text{P}_{4(s)} + 5\text{O}_{2(g)} \rightleftharpoons \text{P}_4\text{O}_{10(s)}$ ? [AIEEE-2004]

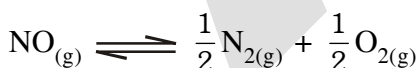
- (1)  $K_C = [\text{P}_4\text{O}_{10}] / [\text{P}_4] [\text{O}_2]^5$
- (2)  $K_C = [\text{P}_4\text{O}_{10}] / 5 [\text{P}_4] [\text{O}_2]$
- (3)  $K_C = [\text{O}_2]^5$
- (4)  $K_C = 1 / [\text{O}_2]^5$

19. For the reaction  $\text{CO}_{(g)} + \text{Cl}_{2(g)} \rightleftharpoons \text{COCl}_{2(g)}$  the  $\frac{K_p}{K_c}$  is equal to - [AIEEE-2004]

- (1)  $\frac{1}{RT}$
- (2)  $RT$
- (3)  $\sqrt{RT}$
- (4) 1.0

20. The equilibrium constant for the reaction

$\text{N}_{2(g)} + \text{O}_{2(g)} \rightleftharpoons 2\text{NO}_{(g)}$  at temperature  $T$  is  $4 \times 10^{-4}$ . The value of  $K_C$  for the reaction



[AIEEE-2004]

- (1)  $2.5 \times 10^2$
- (2) 50
- (3)  $4 \times 10^{-4}$
- (4) 0.02

21. For the reaction equilibrium,

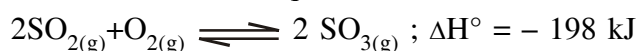
$\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$  the concentration of  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  at equilibrium are  $4.8 \times 10^{-2}$  and  $1.2 \times 10^{-2} \text{ mol L}^{-1}$  respectively. The value of  $K_C$  for the reaction is- [AIEEE-2003]

- (1)  $3 \times 10^{-3} \text{ mol L}^{-1}$
- (2)  $3 \times 10^3 \text{ mol L}^{-1}$
- (3)  $3.3 \times 10^2 \text{ mol L}^{-1}$
- (4)  $3 \times 10^{-1} \text{ mol L}^{-1}$



22. Consider the reaction equilibrium

[AIEEE-2003]



On the basis of Le-Chatelier's principle, the condition favourable for the forward reaction is -

- (1) Lowering the temperature and increasing the pressure
- (2) Any value of temperature as well as pressure
- (3) Lowering of temperature as well as pressure
- (4) Increasing temperature as well as pressure

23. Reaction  $\text{CO}_{(g)} + \frac{1}{2} \text{O}_{2(g)} \rightleftharpoons \text{CO}_{2(g)}$ . The value of  $\frac{K_p}{K_c}$  is -

[AIEEE-2002]

- (1)  $\frac{1}{RT}$
- (2)  $\sqrt{RT}$
- (3)  $\frac{1}{\sqrt{RT}}$
- (4)  $RT$

24. One of the following equilibrium is not affected by change in volume of the flask - [AIEEE-2002]

- (1)  $\text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g)$
- (2)  $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$
- (3)  $\text{N}_2(g) + \text{O}_2 \rightleftharpoons 2\text{NO}(g)$
- (4)  $\text{SO}_2\text{Cl}_2(g) \rightleftharpoons \text{SO}_2(g) + \text{Cl}_2(g)$

J-ADVANCE

- The thermal dissociation equilibrium of  $\text{CaCO}_3(\text{s})$  is studied under different conditions.  
 $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$  [JEE 2013]  
 For this equilibrium, the correct statement(s) is(are)  
 (A)  $\Delta H$  is dependent on T  
 (B) K is independent of the initial amount of  $\text{CaCO}_3$   
 (C) K is dependent on the pressure of  $\text{CO}_2$  at a given T  
 (D)  $\Delta H$  is independent of the catalyst, if any
- If  $\text{Ag}^+ + \text{NH}_3 \rightleftharpoons [\text{Ag}(\text{NH}_3)]^+$ ;  $K_1 = 1.6 \times 10^3$  and [JEE 2006]  
 $[\text{Ag}(\text{NH}_3)]^+ + \text{NH}_3 \rightleftharpoons [\text{Ag}(\text{NH}_3)_2]^+$ ;  $K_2 = 6.8 \times 10^3$ . The formation constant of  $[\text{Ag}(\text{NH}_3)_2]^+$  is :  
 (A)  $6.08 \times 10^{-6}$  (B)  $6.8 \times 10^{-6}$  (C)  $1.6 \times 10^3$  (D)  $1.088 \times 10^7$
- Consider the following equilibrium in a closed container :  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ .  
 At a fixed temperature, the volume of the reaction container is halved. For this change, which of the following statements holds true regarding the equilibrium constant ( $K_p$ ) and degree of dissociation ( $\alpha$ ) : [JEE 2002]  
 (A) Neither  $K_p$  nor  $\alpha$  changes (B) Both  $K_p$  and  $\alpha$  change  
 (C)  $K_p$  changes, but  $\alpha$  does not change (D)  $K_p$  does not change, but  $\alpha$  changes
- At constant temperature, the equilibrium constant ( $K_p$ ) for the decomposition reaction.  
 $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$  is expressed by  $K_p = 4x^2P/(1-x^2)$  where P is pressure, x is extent of decomposition.  
 Which of the following statement is true ? [JEE 2001]  
 (A)  $K_p$  increases with increase of P (B)  $K_p$  increases with increase of x  
 (C)  $K_p$  increases with decrease of x (D)  $K_p$  remains constant with change in P or x
- When 3.06g of solid  $\text{NH}_4\text{HS}$  is introduced into a two litre evacuated flask at  $27^\circ\text{C}$ , 30% of the solid decomposes into gaseous ammonia and hydrogen sulphide. [JEE 2000]  
 (i) Calculate  $K_c$  &  $K_p$  for the reaction at  $27^\circ\text{C}$ .  
 (ii) What would happen to the equilibrium when more solid  $\text{NH}_4\text{HS}$  is introduced into the flask?
- When two reactants A and B are mixed to give products C and D, the reaction quotient Q, at the initial stages of the reaction : [JEE 2000]  
 (A) is zero (B) decrease with time  
 (C) independent of time (D) increases with time
- For the reversible reaction : [JEE 2000]  
 $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$  at  $500^\circ\text{C}$ . The value of  $K_p$  is  $1.44 \times 10^{-5}$ , when partial pressure is measured in atmospheres. The corresponding value of  $K_c$  with concentration in  $\text{mol L}^{-1}$  is :  
 (A)  $1.44 \times 10^{-5} / (0.082 \times 500)^2$  (B)  $1.44 \times 10^{-5} / (8.314 \times 773)^2$   
 (C)  $1.44 \times 10^{-5} / (0.082 \times 500)^2$  (D)  $1.44 \times 10^{-5} / (0.082 \times 773)^2$
- The degree of dissociation is 0.4 at 400K & 1.0 atm for the gaseous reaction  
 $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2(\text{g})$ . Assuming ideal behaviour of all gases. Calculate the density of equilibrium mixture at 400K & 1.0 atm pressure. [JEE 1999]

**ANSWER KEY****EXERCISE # O-I**

- |         |         |         |         |
|---------|---------|---------|---------|
| 1. (D)  | 2. (C)  | 3. (C)  | 4. (C)  |
| 5. (D)  | 6. (B)  | 7. (C)  | 8. (B)  |
| 9. (C)  | 10. (B) | 11. (A) | 12. (C) |
| 13. (A) | 14. (B) | 15. (A) | 16. (C) |
| 17. (B) | 18. (A) | 19. (B) | 20. (A) |
| 21. (D) | 22. (B) | 23. (D) | 24. (C) |
| 25. (B) | 26. (B) | 27. (B) | 28. (A) |
| 29. (C) | 30. (C) | 31. (B) | 32. (C) |
| 33. (A) | 34. (D) | 35. (A) | 36. (A) |
| 37. (C) | 38. (A) | 39. (D) | 40. (A) |

**J-MAIN**

- |              |             |             |             |
|--------------|-------------|-------------|-------------|
| 1. Ans.(4)   | 2. Ans.(4)  | 3. Ans(3)   | 4. Ans(1)   |
| 5. Ans(2)    | 6. Ans(2)   | 7. Ans(4)   | 8. Ans(1)   |
| 9. Ans(3)    | 10. Ans.(1) | 11. Ans.(3) | 12. Ans.(1) |
| 13. Ans.(4)  | 14. Ans.(4) | 15. Ans.(2) | 16. Ans.(3) |
| 17. Ans.(2). | 18. Ans.(4) | 19. Ans.(1) | 20. Ans.(2) |
| 21. Ans.(1)  | 22. Ans.(1) | 23. Ans.(3) | 24. Ans.(3) |

**J-ADVANCE**

- |                |            |            |            |
|----------------|------------|------------|------------|
| 1. Ans.(A,B,D) | 2. Ans.(D) | 3. Ans.(D) | 4. Ans.(D) |
|----------------|------------|------------|------------|
5. (i)  $K_c = 8.1 \times 10^{-5} \text{ mol}^2 \text{ L}^2$ ;  $K_p = 4.91 \times 10^{-2} \text{ atm}^2$  (ii) No effect;
6. Ans.(D)
7. Ans.(D)
8. Ans.  $4.54 \text{ g dm}^{-3}$

**NURTURE COURSE**

**REAL GAS**

## REAL GAS

### 1. Introduction :

An ideal gas is a hypothetical gas whose pressure, volume and temperature behaviour is completely described by the ideal gas equation. Actually no gas is ideal or perfect in nature. All gases are real gases.

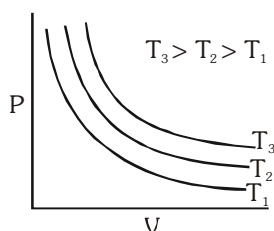
Real gases do not obey the ideal gas laws exactly under all conditions of temperature and pressure. Real gases deviates from ideal behaviour because of mainly two assumptions of "Kinetic theory of gases".

- (i) The volume of gas particle is negligible compared to volume of container (while the real gas particle may have some significant volume).
- (ii) There is no interaction between gaseous particles (while attraction forces exist between real gas particles).

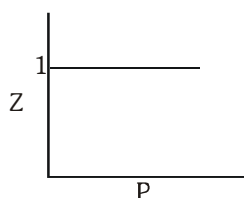
### 1.1 Comparision between Real and Ideal gas :

#### IDEAL GAS

- (i)  $PV = nRT$
- (ii) No liquifaction is possible.

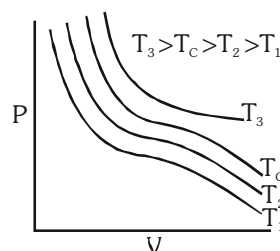


(iii)



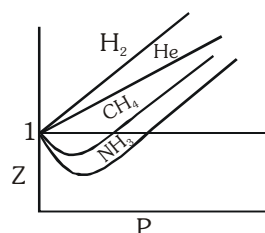
#### REAL GAS

- (i)  $PV \neq nRT$   
 $\Rightarrow$  If  $PV > nRT$  (Gas is less compressible than ideal gas).  
 If  $PV < nRT$  (Gas is more compressible than ideal gas).
- (ii) Liquifaction is possible below a certain temperature.



$\Rightarrow$  Follow critical phenomena and can not liquefy above  $T_c$ .

(iii)



- (iv) No interaction force is present between gas particles.      (iv) Interaction force exist between gas particles which vary depending upon conditions.
- (v) Volume of gas particles is negligible w.r.t. volume of container.      (v) Volume of gas particles has significant value and can not be neglected normally w.r.t. volume of container.

## 1.2 VANDER WAAL EQUATION OF REAL GASES

The ideal gas equation does not consider the effect of attractive forces and molecular volume.

Van der Waal corrected the ideal gas equation by taking the effect of

- (a) Molecular volume
- (b) Molecular attraction

## (A) Volume correction :

In the ideal gas equation,  $P_i V_i = nRT$ ,  $V_i$  represents the ideal volume where the molecules can move freely. In real gases, a part of the total volume is occupied by the gas molecules. Hence the free volume  $V_i$  is the total volume  $V$  minus the volume occupied by the gas molecules.

Real volume of gas = Actual volume of container – volume occupied by molecules in motion.

$$V_i = V - nb \text{ for } n \text{ mole of gas}$$

Where  $b$  is termed the 'excluded volume' or 'co-volume' per mole.

It is constant and characteristic for each gas.

$$b = 4 \times \text{volumes of one molecules} \times N_A$$

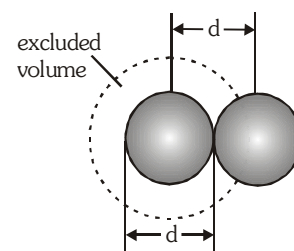
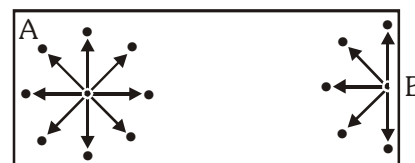


Illustration of excluded volume

## (B) Pressure correction :

In order to take account the effect of intermolecular forces of attraction, let us consider a molecule A in the midst of the vessel.

This molecule is surrounded by other molecules in a symmetrical manner and is being attracted uniformly on all sides by the neighbouring molecules with the result that this molecule on the whole experiences no net force of attraction.



Now, consider a molecule B near the side of the vessel, which is about to strike one of its sides, thus contributing towards the total pressure of the gas. There are molecules only in one side of the vessel, i.e. towards its centre, with the result of that, this molecule experiences a net force of attraction towards the centre of the vessel. This results in decreasing the velocity of the molecule, and hence its momentum. Thus, the molecule does not contribute as much force as it would have, had there been no force of attraction. Thus, the pressure of a real gas would be smaller than the corresponding pressure of an ideal gas.

Van der Waals noted that the total force of attraction on any molecule about to hit a wall is proportional to the concentration of neighbouring molecules,  $n/V$ . However, the number of molecules about to hit the wall per unit wall area is also proportional to the concentration  $n/V$ . Therefore, the force per unit wall area, or pressure, is reduced from that assumed in the ideal gas wall by a factor proportional to  $n^2/V^2$ . Letting  $a$  be the proportionality constant, we can write

$$P(\text{actual}) = P(\text{ideal}) - \frac{an^2}{V^2} \quad \text{or} \quad P(\text{ideal}) = P(\text{actual}) + \frac{an^2}{V^2}$$

'a' is a constant which depends upon the nature of the gas,

Combining the two corrections,  
for 1 mole of gas

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

and for  $n$  mole of gas  $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$

**The constants 'a' and 'b' :**

Van der Waals constant for attraction 'a' and volume 'b' are characteristic constants for a given gas.

- (i) The 'a' values for a given gas are measure of intermolecular forces of attraction. More are the intermolecular forces of attraction, more will be the value of a.
- (ii) The gas having higher value of 'a' can be liquefied easily and therefore  $H_2$  and He are not liquefied easily.
- (iii) Unit of 'a' is  $\text{atm lit}^2 \text{mole}^{-2}$  or  $\text{dyne cm}^4 \text{mole}^{-2}$  or  $\text{Nm}^4 \text{mol}^{-2}$
- (iv) Unit of 'b' is  $\text{lit mole}^{-1}$  or  $\text{cm}^3 \text{mole}^{-1}$  or  $\text{m}^3 \text{mol}^{-1}$



**The van der Waals constants for some common gases**

| Gas               | a ( $\text{atmL}^2 \text{mol}^{-2}$ ) | b ( $\text{L mol}^{-1}$ ) |
|-------------------|---------------------------------------|---------------------------|
| Ammonia           | 4.17                                  | 0.0371                    |
| Argon             | 1.35                                  | 0.0322                    |
| Carbon dioxide    | 3.59                                  | 0.0427                    |
| Carbon monoxide   | 1.49                                  | 0.0399                    |
| Chlorine          | 6.49                                  | 0.0562                    |
| Ethane            | 5.49                                  | 0.0638                    |
| Ethanol           | 2.56                                  | 0.087                     |
| Ethylene          | 4.47                                  | 0.0571                    |
| Helium            | 0.034                                 | 0.0237                    |
| Hydrogen          | 0.024                                 | 0.0266                    |
| Hydrogen chloride | 3.67                                  | 0.0408                    |
| Hydrogen bromide  | 4.45                                  | 0.0433                    |
| Methane           | 2.25                                  | 0.0428                    |
| Neon              | 0.21                                  | 0.0171                    |
| Nitric oxide      | 1.34                                  | 0.0279                    |
| Nitrogen          | 1.39                                  | 0.0319                    |
| Oxygen            | 1.36                                  | 0.0318                    |
| Sulphur dioxide   | 3.71                                  | 0.0564                    |
| Water             | 5.44                                  | 0.0305                    |

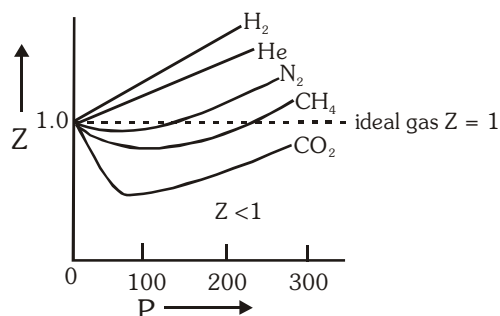
### 1.3 COMPRESSIBILITY FACTOR (Z) :

The extent to which a real gas departs from the ideal behaviour may be expressed in terms of compressibility factor (Z),

$$Z = \frac{(PV)_{\text{real}}}{(PV)_{\text{ideal}}} = \frac{V_m}{V_{m(\text{ideal})}} = \frac{PV_m}{RT} \quad [V_m = \text{molar volume}]$$

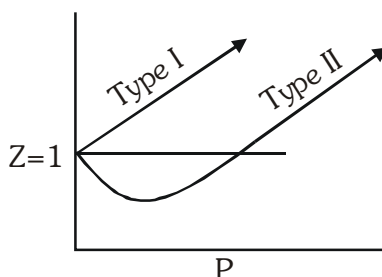
### 1.4 Plots of compressibility factor vs pressure :

- For an ideal gas  $Z = 1$  and is independent of temperature and pressure.
- Exceptional behaviour of  $\text{H}_2$  and He :  
For these gases  $Z > 1$  at  $0^\circ\text{C}$ .
- Effect of pressure :  
At very low P,  $PV_m \approx RT$  i.e.  $Z \approx 1$   
At low P,  $PV_m < RT$  i.e.  $Z < 1 \Rightarrow$  attractive forces dominant  
At high P,  $PV_m > RT$  i.e.  $Z > 1 \Rightarrow$  repulsive forces dominant
- For the gases which are easily liquefied (e.g.  $\text{CO}_2$ ) Z dips sharply below the ideal line in the low pressure region.
- Effect of temperature : An increase in temperature shows a decrease in deviation from ideal behaviours, Z approaches unity with increase in temperature.



### 1.5 Verification of compressibility factor using Van Der Waal's equation :

Variation of Z with P for real gas at any temperature is given by following graph.



Van der waal equation :

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT$$



(i) At low pressure and constant temperature

At low pressure  $V_m$  will be high hence  $b$  can be neglected in comparison to  $V_m$ . But  $\frac{a}{V_m^2}$  can't be neglected as pressure is low. Thus equation would be

$$\left(P + \frac{a}{V_m^2}\right)V_m = RT$$

$$PV_m + \frac{a}{V_m} = RT$$

$$\frac{PV_m}{RT} + \frac{a}{V_m RT} = 1$$

$$Z = 1 - \frac{a}{V_m RT} \Rightarrow Z < 1$$

Substituting  $V_m = \frac{RT}{P}$  in above equation ;  $Z = 1 - \frac{aP}{R^2 T^2}$

At low pressure, real gas is easily compressible as compared to an ideal gas.

(ii) At high pressure and constant temperature

At high pressure the  $V_m$  will be low. So  $b$  can't be neglected in comparison to  $V_m$  but  $\frac{a}{V_m^2}$  can be neglected as compared to much higher values of  $P$ .

Then van der Waals' equation will be

$$P(V_m - b) = RT$$

$$PV_m - Pb = RT$$

$$\frac{PV_m}{RT} = \frac{Pb}{RT} + 1$$

$$Z = \frac{Pb}{RT} + 1 \Rightarrow (Z > 1)$$

At high pressure, gas is more difficult to compress as compared to an ideal gas.

(iii) At low pressure and very high temperature.

$V_m$  will be very large, hence 'b' can be neglected and  $\frac{a}{V_m^2}$  can also be neglected as  $V_m$  is very large.

$$PV_m = RT \text{ (ideal gas condition)}$$

(iv) For  $H_2$  or He  $a \approx 0$  because molecules are smaller in size or vander Waal's forces will be very weak.

$$P(V_m - b) = RT$$

So  $Z = 1 + \frac{Pb}{RT}$

This explains type I plot.

**Ex.1.** Calculate the pressure exerted by 5 mole of  $\text{CO}_2$  in one litre vessel at  $47^\circ\text{C}$  using van der waal's equation. Also report the pressure of gas if it behaves ideal in nature.

Given that  $a = 3.592 \text{ atm L}^2 \text{ mol}^{-2}$ ,  $b = 0.0427 \text{ L/mol}$ . Also, if the volume occupied by  $\text{CO}_2$  molecules is negligible, then calculate the pressure exerted by one mole of  $\text{CO}_2$  gas at  $273 \text{ K}$ .

**Sol.** Vander waal's equation

$$\left[ p + \frac{n^2 a}{V^2} \right] [V - nb] = nRT$$

$$n_{\text{CO}_2} = 5, V = 1 \text{ litre}, T = 320 \text{ K}, a = 3.592, b = 0.0427$$

$$\therefore \left[ P + 25 \times \frac{3.592}{1} \right] [1 - 5 \times 0.0427] = 5 \times 0.0821 \times 320$$

$$\therefore P = 77.218 \text{ atm}$$

For ideal behaviour of gas,  $PV = nRT$

$$\therefore P \times 1 = 5 \times 0.0821 \times 320$$

$$\therefore P = 131.36 \text{ atm}$$

For one mole  $\left[ P + \frac{a}{V^2} \right] [V - b] = RT$

$$\therefore P = \frac{RT}{V} - \frac{a}{V^2}$$

$$\therefore P = \frac{0.0821 \times 273}{22.4} - \frac{3.592}{(22.4)^2}$$

$$\therefore P = 0.9922 \text{ atm}$$

The volume occupied by 1 mole at  $273 \text{ K}$  is  $22.4 \text{ litre}$  if  $b$  is negligible.

**Ex.2** One mole of  $\text{CCl}_4$  vapours at  $77^\circ\text{C}$  occupies a volume of  $35.0 \text{ L}$ . If vander waal's constants are  $a = 20.39 \text{ L}^2 \text{ atm mol}^{-2}$  and  $b = 0.1383 \text{ L mol}^{-1}$ , calculate compressibility factor  $Z$  under,

(a) low pressure region.

(b) high pressure region.

**Sol.** (a) Under low pressure region,  $V$  is high

$$\therefore (V - b) \approx V$$

$$\left( P + \frac{a}{V^2} \right) V = RT$$

$$PV + \frac{a}{V} = RT$$

$$\frac{PV}{RT} + \frac{a}{RTV} = 1$$

$$Z = \frac{PV}{RT} = \left( 1 - \frac{a}{RTV} \right) = 1 - \frac{20.39}{0.0821 \times 350 \times 35} = 0.98$$

(b) Under high pressure region,  $P$  is high,

$$\left( P + \frac{a}{V^2} \right) \approx P$$

$$\therefore P(V - b) = RT$$

$$PV - Pb = RT$$

$$\frac{PV}{RT} - \frac{Pb}{RT} = 1$$

$$\therefore Z = \frac{PV}{RT} = 1 + \frac{Pb}{RT} \quad \left( \because \frac{PV}{RT} = 1, \text{ or } \frac{P}{RT} = \frac{1}{V} \right)$$

$$Z = 1 + \frac{b}{V} = 1 + \frac{0.1383}{35} = 1 + 0.004 = 1.004$$

**Ex.3** One way of writing the equation of state for real gases is  $PV = RT \left[ 1 + \frac{B}{V} + \dots \right]$  where B is a constant. Derive an approximate expression for B in terms of van der Waal's constants a and b.

**Sol.** According to van der Waal's equation

$$\left[ P + \frac{a}{V^2} \right] [V - b] = RT \text{ or } P = \frac{RT}{(V-b)} - \frac{a}{V^2}$$

Multiply by V, then

$$PV = \frac{RTV}{(V-b)} - \frac{a}{V} \quad \text{or} \quad PV = RT \left[ \frac{V}{V-b} - \frac{a}{VRT} \right]$$

$$\text{or } PV = RT \left[ \left( 1 - \frac{b}{V} \right)^{-1} - \frac{a}{VRT} \right]$$

$$\therefore \left[ 1 - \frac{b}{V} \right]^{-1} = 1 + \frac{b}{V} + \left( \frac{b}{V} \right)^2 + \dots$$

$$\therefore PV = RT \left[ 1 + \frac{b}{V} + \dots - \frac{a}{VRT} \right]$$

$$PV = RT \left[ 1 + \left( b - \frac{a}{RT} \right) \cdot \frac{1}{V} + \dots \right]$$

$$\therefore B = b - \frac{a}{RT}$$

## 2. BOYLE TEMPERATURE :

(i) It is temperature at which a real gas behave ideally in a wide range of pressure.

(ii) (a) Temperature < Boyle temperature

$Z < 1$ , low pressure range

$Z > 1$ , high pressure range

(b) Temperature = Boyle temperature

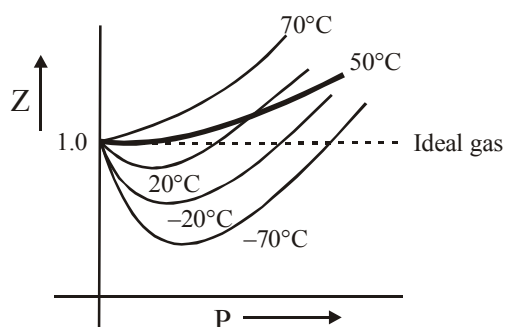
$Z = 1$ , low pressure range

$Z > 1$ , high pressure range

(c) At temperature > Boyle temperature

$Z > 1$ , at all pressure

(d)  $T \rightarrow \infty, Z \rightarrow 1$



On increasing the temperature, the thermal energy increases and simultaneously the attractive forces decreases. Hence a temperature comes at which the thermal energy become too high that it balances the effect of attraction and gas molecules becomes independent.

If at Boyle temperature, pressure is increased, molecules come more closer. Due to repulsive force,  $Z$  becomes greater than 1.

## 2.1 CALCULATION OF $T_B$ :

$$(i) \quad PV_m = RT = \left( 1 + \frac{B}{V_m} + \underbrace{\frac{C}{V_m^2}}_{\text{negligible}} + \dots \right) \text{ at low pressure.}$$

At  $T = T_B$ , the second initial coefficient should be 0

$$B = 0$$

$$\text{or} \quad b - \frac{a}{RT_B} = 0$$

$$\therefore \quad \boxed{T_B = \frac{a}{Rb}}$$

(ii) Calculus method :

$$\text{At Boyle temperature, } \left( \frac{\partial Z}{\partial P} \right)_T = 0 \text{ at low pressure.}$$

**Ex.4** Derive the expression for compressibility factor of a vanderwaal gas at Boyle temperature.

**Solution :**  $Z = \frac{V_m}{V_m - b} - \frac{a}{V_m - RT}$

At Boyle temperature,

$$Z = \frac{V_m}{V_m - b} - \frac{a}{V_m R \times \frac{a}{Rb}}$$

$$Z = \frac{V_m}{V_m - b} - \frac{b}{V_m}$$

$$Z = \frac{V_m^2 - V_m b + b^2}{V_m (V_m - b)}$$

$$Z = 1 + \frac{b^2}{V_m (V_m - b)}$$

**Ex.5** Calculate the volume occupied by 2 moles of a vanderwall gas at 5 atm 800 K.

Given :  $a = 4.0 \text{ atm } \ell^2 \text{ mol}^{-2}$ ,  $b = 0.0625 \text{ } \ell \text{ mol}^{-1}$ ,  $R = 0.08 \text{ } \ell \text{-atm/K-mol}$

**Solution :**  $T_B = \frac{a}{Rb} = 800\text{K}$

Gas behave ideally at given condition.

$$PV = nRT$$

$$5 \times V = 2 \times 0.08 \times 800$$

$$V = 25.6 \text{ litre}$$

### 3. LIQUEFACTION OF GASES AND CRITICAL POINTS

The phenomenon of converting a gas into liquid is known as liquefaction. The liquefaction of a gas takes place when the intermolecular forces of attraction become so high that they exist in liquid state. A gas can be liquefied by :

- Increasing pressure** : An increase in pressure results decrease in intermolecular distance.
- Decreasing temperature** : A decrease in temperature results decrease in kinetic energy of molecules.

**Note** : Due to absence of intermolecular forces, ideal gases can never be liquified.

#### 3.1 Andrews Isotherms :

The essential conditions for liquefaction of gases were discovered by Andrews (1869) as a result of his study of P–V–T relationship for  $\text{CO}_2$ . The types of isotherms are shown in figure.

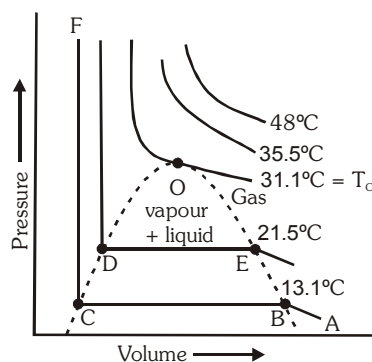


Fig : Isotherms for carbon dioxide

#### Observations from figure :

- At low temperatures** : For the curve ABCF, as the pressure increases, volume of the curve decreases (curve A to B). At point B, at constant pressure, liquefaction commences and the volume decreases rapidly (because gas is converted to liquid with higher density). At point C, liquefaction is complete. The line CF represents the variation of V with P of the liquid state. The steepness of the line CF indicates that the liquid cannot be easily compressed. Thus AB, represent gaseous state, BC represent liquid and vapour in equilibrium and CF represent liquid state.

The pressure corresponding to the line BC is vapour pressure of the liquid at that temperature.

- At lower temperatures** : Similar type of curve as in case (A) is obtained but the width of the horizontal portion is reduced. The pressure corresponding to this portion is higher than at lower temperatures.
- At high temperatures** : (say  $48^\circ\text{C}$ ), the isotherms are like those of ideal gas. Gas does not liquify, even at very high pressure.
- At temperature ( $31.1^\circ\text{C}$ )** : The horizontal portion is reduced to a point.

The isotherm at  $T_c$  is called **critical isotherm**.

At point O,  $\frac{dP}{dV} = 0$ .

The point O is called the **point of inflection**.

#### 3.2 Critical parameters or critical constants :

**Critical temperature ( $T_c$ )** : The temperature above which a system can never be liquefied by the application of pressure alone i.e. the temperature above which a liquid cannot exist is called the critical temperature  $T_c$ .

**Critical pressure ( $P_C$ )** : The minimum pressure required to liquefy the system at the temperature  $T_C$  is called the critical pressure  $P_C$ .

**Critical volume ( $V_C$ )** : The volume occupied by one mole of the system at critical temperature,  $T_C$  and critical pressure,  $P_C$  is called the critical volume ( $V_C$ ) of the gas.

### 3.3 Determination of value of $P_C$ , $V_C$ and $T_C$ :

The Vander waal's equation is

$$\left(P + \frac{a}{V_m^2}\right) (V_m - b) = RT$$

or  $V_m^3 - \left(b + \frac{RT}{P}\right) V_m^2 + \frac{a}{P} V_m - \frac{ab}{P} = 0 \quad \dots (1)$

This equation has three roots in  $V_m$  for given values of  $a$ ,  $b$ ,  $P$  and  $T$ . It is found that either all the three roots are real or one is real and the other two are imaginary.

At temperature lower than  $T_C$ , the isotherm exhibits a maximum and a minimum for certain values of pressures, the equation gives three roots of volume e.g.,  $V_1$ ,  $V_2$  and  $V_3$  at pressure  $P_1$ . On increasing the temperature, the three roots become closer to each other and ultimately at critical temperature, they become identical. Thus, the cubic equation  $V_m$  can be written as

$$(V_m - V') (V_m - V'') (V_m - V''') = 0$$

At the critical point  $V' = V'' = V''' = V_C$

$\therefore$  the equation becomes,

$$(V_m - V_C)^3 = 0$$

or  $V_m^3 - V_C^3 - 3V_C V_m^2 + 3V_C^2 V_m = 0 \quad \dots (2)$

By comparing the coefficients in eq.(1) and eq(2)

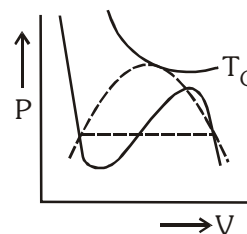
$$3V_C = b + \frac{RT_C}{P_C}, \quad 3V_C^2 = \frac{a}{P_C}, \quad V_C^3 = \frac{ab}{P_C}$$

By solving,  $V_C = 3b$ ,  $P_C = \frac{a}{27b^2}$  and  $T_C = \frac{8a}{27Rb}$

- The value of critical compressibility factor in terms of vander wall's constants is given by

$$Z = \frac{P_C V_C}{RT_C} = \frac{\frac{a}{27b^2} \times 3b}{R \times \frac{8b}{27Rb}} = \frac{3}{8} = 0.375$$

If we compare the value of  $\frac{P_C V_C}{RT_C} = 0.375$ , with the experimental values, it has been found that the agreement is very poor.



Critical constants of gases

| Gas                           | $P_C$ (atm) | $V_{m,c}$ (cm <sup>3</sup> mol <sup>-1</sup> ) | $T_C$ (K) |
|-------------------------------|-------------|------------------------------------------------|-----------|
| He                            | 2.26        | 57.9                                           | 5.2       |
| Ne                            | 26.9        | 41.7                                           | 44.4      |
| Ar                            | 48.1        | 75.2                                           | 150.7     |
| Xe                            | 58.0        | 119.0                                          | 289.7     |
| H <sub>2</sub>                | 12.8        | 65.5                                           | 33.3      |
| O <sub>2</sub>                | 50.1        | 78.2                                           | 154.8     |
| N <sub>2</sub>                | 33.5        | 90.1                                           | 126.2     |
| CO <sub>2</sub>               | 72.8        | 94.0                                           | 304.2     |
| H <sub>2</sub> O              | 218.0       | 55.6                                           | 647.3     |
| NH <sub>3</sub>               | 111.5       | 72.5                                           | 405.0     |
| CH <sub>4</sub>               | 45.6        | 98.7                                           | 190.6     |
| C <sub>2</sub> H <sub>6</sub> | 48.2        | 148.0                                          | 305.4     |

**Ex.6** The critical temperature and pressure of CO<sub>2</sub> gas are 304.2 K and 72.9 atm respectively. What is the radius of CO<sub>2</sub> molecule assuming it to behave as vander Waal's gas ?

**Sol.**  $T_C = 304.2$  K  $P_C = 72.9$  atm

$$T_C = \frac{8a}{27Rb} \quad P_C = \frac{a}{27b^2}$$

$$\therefore \frac{T_C}{P_C} = \frac{\frac{8a}{27Rb}}{\frac{a}{27b^2}} = \frac{8a}{27Rb} \times \frac{27b^2}{a} = \frac{8b}{R}$$

$$\text{or } b = \frac{RT_C}{8P_C} = \frac{1}{8} \times \frac{0.082 \times 304.2}{72.9} = 0.04277 \text{ lit mol}^{-1}$$

$$b = 4 N_A \times \frac{4}{3} \pi r^3 = 42.77 \text{ cm}^3$$

$$\text{or } r = (4.24)^{1/3} \times 10^{-8} \text{ cm} = 1.62 \times 10^{-8} \text{ cm}$$

$$\therefore \text{radius of CO}_2 \text{ molecule} = 1.62 \text{ \AA}$$

#### 4. THE LIQUID STATE

Liquid state is intermediate between gaseous and solid states. The liquids possess fluidity like gases but incompressibility like solids.

The behaviour of liquids explained above gives some characteristic properties to the liquids such as definite shape, incompressibility, diffusion, fluidity (or viscosity), evaporation (or vapour pressure), surface tension, etc.

The following general characteristics are exhibited by liquids :

(i) **Shape :**

Liquids have no shape of their own but assume the shape of the container in which they are kept. No doubt, liquids are mobile but they do not expand like gases as to fill up all the space offered to them but remain confined to the lower part of the container.

(ii) **Volume :**

Liquids have definite volume as the molecules of a liquid are closely packed and the cohesive forces are strong.

(iii) **Density :**

As the molecules in liquids are closely packed, the densities of liquids are much higher than in gaseous state. For example, density of water at 100° C and 1 atmospheric pressure is 0.958 g mL<sup>-1</sup> while that of water vapour under similar conditions as calculated from ideal gas law  $\left(d = \frac{MP}{RT}\right)$  is 0.000588 g mL<sup>-1</sup>.

(iv) **Compressibility :**

The molecules in a liquid are held in such close contact by their mutual attractive forces (cohesive forces) that the volume of any liquid decreases very little on increasing pressure. Thus, liquids are relatively incompressible compared to gases.

(v) **Diffusion :**

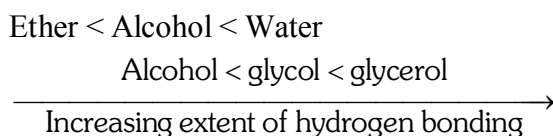
When two miscible liquids are put together, there is slow mixing as the molecules of one liquid move into the other liquid. As the space available for movement of molecules in liquids is much less and their velocities are small. Liquids diffuse slowly in comparison to gases.

(vi) **Evaporation :**

The process of changes of liquid into vapour state on standing is termed **evaporation**. Evaporation may be explained in terms of motion of molecules. At any given temperature all the motion of molecules do not possess the same kinetic energy (average kinetic energy is, however same). Some molecules move slowly, some at intermediate rates and some move very fast. A rapidly moving molecule near the surface of the liquid may possess sufficient kinetic energy to overcome the attraction of its neighbours and escape. Evaporation depends on the following factor.



(a) **Nature of the liquid :** The evaporation depends on the strength of intermolecular forces (cohesive forces). The liquids having low intermolecular forces evaporate faster in comparison to the liquids having high intermolecular forces. For example, ether evaporates more quickly than alcohol, and alcohol evaporates more quickly than water, as the intermolecular forces in these liquids are in the order :



(b) **Surface area :** Evaporation is a surface phenomenon. Larger the surface area, greater is the opportunity of the molecules to escape. Thus, rate of evaporation increases with increase of surface area.

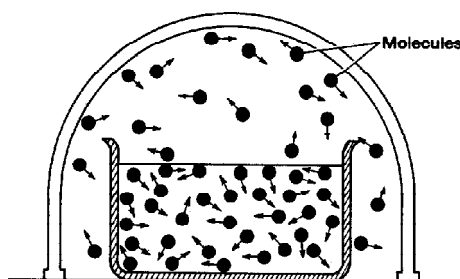
(c) **Temperature :** Rate of evaporation increases with the increase of temperature as the kinetic energy of the molecules increases with the rise of temperature.

(d) **Flow of air current over the surface :** Flow of air helps the molecules to go away from the surface of liquid and, therefore, increases the evaporation of liquid in open vessel.

(vii) **Heat of vaporisation :**

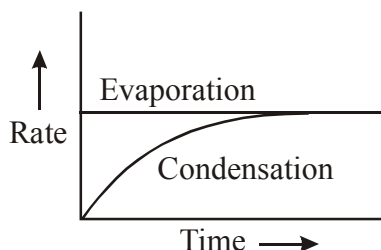
The quantity of heat required to evaporate a unit mass of a given liquid at constant temperature is known as heat of vaporisation. The heat of vaporisation depends on the strength of the intermolecular forces with in the liquid. The value of heat of vaporisation generally decreases with increase in temperature. It becomes zero at the critical temperature. When the vapour is condensed into a liquid, heat is evolved. This is called **heat of condensation**. It is numerically equal to the heat of vaporisation at the same temperature.

(viii) **Vapour pressure :**



When the space above the liquids is closed, the molecules cannot escape into open but strike the walls of the container, rebound and may strike the surface of the liquid, where they may be trapped. The return of the molecules from the vapour state of the liquid state is known as **condensation**. As evaporation proceeds, the number of molecules in the vapour state increases and, in turn, the rate of condensation increases.

The rate of condensation soon becomes equal to the rate of the evaporation, i.e., the vapour in the closed container is in equilibrium with the liquid.



At equilibrium the concentration of molecules in the vapour phase remains unchanged. The pressure exerted by the vapour in equilibrium with liquid, at a given temperature, is called the **vapour pressure**. Mathematically, it may be given by ideal gas equation, assuming ideal behaviour.

$$P = \frac{n}{V} RT = CRT$$

where  $C$  is the concentration of vapour, in mol/litre.

Since the rate of evaporation increases and rate of condensation decreases with increasing temperature, vapour pressure of liquids always increases as temperature increases. At any given temperature, the vapour pressures of different liquids are different because their cohesive forces are different. Easily vaporisable liquids are called **volatile liquids** and they have relatively high vapour pressure. Vapour pressure values (in mm of Hg) for water, alcohol and ether at different temperatures are given in the following table :

| Substance     | Temperatures |       |       |        |        |
|---------------|--------------|-------|-------|--------|--------|
|               | 0° C         | 20° C | 40° C | 80° C  | 100° C |
| Water         | 4.6          | 17.5  | 55.0  | 355.5  | 760.3  |
| Ethyl alcohol | 12.2         | 43.9  | 812.6 | 1693.3 |        |
| Diethyl ether | 185.3        | 442.2 | 921.1 | 2993.6 | 4859.4 |

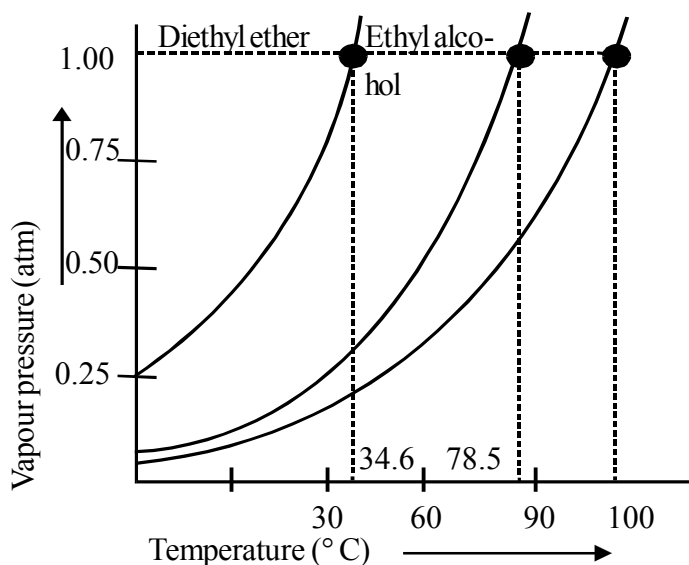
The vapour pressure of a given liquid at two different temperatures can be compared with the help of **Clausius-Clapeyron equation**.

$$\log \times \frac{P_2}{P_1} = \frac{\Delta H}{2.303R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

Where  $\Delta H$  is the latent heat of vaporisation and  $R$  is the molar gas constant.

**(ix) Boiling point :**

The temperature at which the vapour pressure of the liquid becomes equal to the atmospheric pressure is called the **boiling point** of the liquid. When a liquid is heated under a given applied pressure, bubbles of vapour begin to form below the surface of the liquid. They rise to the surface and burst releasing the vapour into the air. This process is called **boiling**. The normal boiling point is the temperature at which the vapour pressure of a liquid is equal to exactly one atmospheric pressure (760 mm of Hg). Figure shows that normal boiling points of di-ethyl ether, ethyl alcohol and water are 34.6° C, 78.5° C and 100° C respectively.



The temperature of the liquid remains constant until all the liquid has been vaporised. Heat must be added to the boiling liquid to maintain the temperature because in the boiling process, the high energy molecules are lost by the liquid.

The boiling point of a liquid changes with the change in external pressure. A liquid may boil at temperatures higher than normal under external pressures greater than one atmosphere; conversely, the boiling point of a liquid may be lowered than normal below one atmosphere. Thus, at high altitudes where the atmospheric pressure is less than 760 mm, water boils at temperatures below its normal boiling water.

Boiling and evaporation are similar processes (conversion of liquid into vapour) but differ in following respects :

- Evaporation takes place spontaneously at all temperatures but boiling occurs at a particular temperature at which the vapour pressure is equal to the atmospheric pressure.
- Evaporation is surface phenomenon. It occurs only at the surface of the liquid whereas boiling involves formation of bubbles below the surface of the liquid.

**Note. :** Boiling does not occur when liquid is heated in a closed vessel.

#### (x) Freezing point :

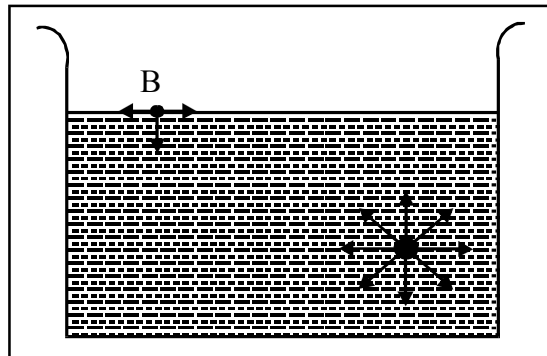
When a liquid is cooled, the kinetic energy of the molecules goes on decreasing. A stage comes when the intermolecular forces become stronger and the rotational motion is seized. At this stage, the formation of solid begins and the liquid is seen to freeze out. The point (temperature) at which the vapour pressure of solid and liquid forms of a substance become equal is termed as **freezing point**.

**Normal freezing point** of a liquid is the temperature at which liquid and solid forms are in equilibrium with each other under a pressure of one atmosphere. The freezing point of a liquid is the same as the melting point of its solid. The amount of heat that must be removed to freeze a unit mass of the liquid at the freezing point, which is called the **heat of fusion**.

The freezing point of a liquid is affected by the change of external pressure. With increased external pressure, the freezing point of some liquids rises while of others falls. But the effect of pressures is very small because solid as well as liquid are almost incompressible.

**(xi) Surface tension :**

It is the property of liquids caused by the intermolecular attractive forces. A molecule within the bulk of the liquid is attracted equally in all the directions by the neighbouring molecules. The resultant force on any one molecule in the centre of the liquid is, therefore, zero. However, the molecules on the surface of the liquid are attracted only inward and sideways. This unbalanced molecular attraction pulls some of the molecules into the bulk of the liquid, i.e., are pulled inward and the surface area is minimized.



**Surface tension is a measure of this inward force on the surface of the liquid. It acts downwards perpendicular to the plane of the surface.** The unit of surface tension is  $\text{dyne cm}^{-1}$ . Surface tension is, thus, defined as **the force acting on the surface at right angles to any line of unit length.**

As the intermolecular forces of attraction decreases with the rise of temperature, the surface tension of a liquid, thus, decreases with increase in temperature. Similarly, addition of chemicals to a liquid may reduce its surface tension. For example, addition of chemicals like soaps, detergents, alcohol, camphor, etc., lowers the surface tension of water.

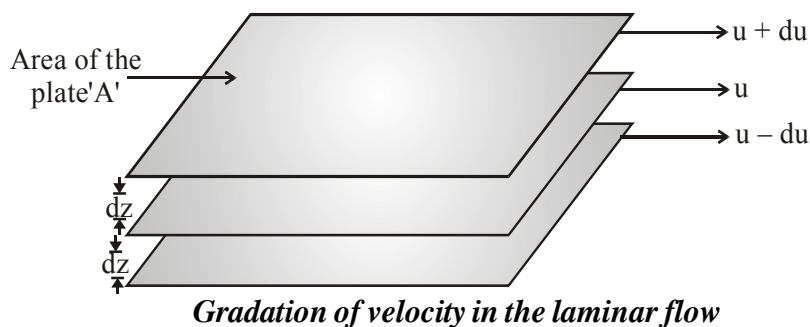
Many common phenomenon can be explained with the help of surface tension. Some are described here :

- (a) **Small droplets are spherical in shape :** The surface tension acting on the surface of the liquid tries to minimise the surface area of a given mass of a liquid. It is known that for a given volume, a sphere has the minimum surface area. On account of this, drops of liquids acquire a spherical shape.
- (b) **Insects can walk on the surface of water :** Many insects can walk on the surface of water without drowning. This is due to the existence of surface tension. The surface tension makes the water surface to behave like an elastic membrane and prevents the insects from drowning.
- (c) **Cleaving action of soap and detergents :** Soap and detergent solutions due to their lower surface tensions penetrate into the fibre and surround the greasy substances and wash them away.
- (d) **Capillary action :** The tendency of a liquid to rise into narrow pores and tiny openings is called capillary action. The liquids rise in the capillary tubes due to the surface tension.
- (e) **Surface Energy :** The work required to be done to increase or extend surface area by unit area is called surface energy. The units of surface energy are, therefore, erg per sq. cm (or joule per sq. metre, i.e.  $\text{J m}^{-2}$  in S.I. system)

**(xii) Viscosity :**

It is one of the characteristic properties of liquids. Viscosity is a measure of resistance to flow which arises due to the internal friction between layers of fluid as they slip past one another while liquid flows. Strong intermolecular forces between molecules hold them together and resist movement of layers past one another.

When a liquid flows over a fixed surface, the layer of molecules in the immediate contact of surface is stationary. The velocity of upper layers increase as the distance of layers from the fixed layer increases. This type of flow in which there is a regular gradation of velocity in passing from one layer to the next is called **laminar flow**. If we choose any layer in the flowing liquid, the layer above it accelerates its flow and the layer below this retards its flow.



If the velocity of the layer at a distance  $dz$  is changed by a value  $du$  then velocity gradient is given by the amount  $\frac{du}{dz}$ . A force is required to maintain the flow of layers. This force is proportional to the area of contact of layers and velocity gradient i.e.

$F \propto A$  ( $A$  is the area of contact)

$F \propto A \frac{du}{dz}$  (where,  $\frac{du}{dz}$  is velocity gradient; the change in velocity with distance)

$$F \propto A \cdot \frac{du}{dz} \Rightarrow F = \eta A \frac{du}{dz}$$

' $\eta$ ' is proportionality constant and is called **coefficient of viscosity**. Viscosity coefficient is the force when velocity gradient is unity and the area of contact is unit area. Thus ' $\eta$ ' is measure of viscosity. SI unit of viscosity coefficient is 1 newton second per square metre ( $\text{N s m}^{-2}$ ) = pascal second ( $\text{Pa s} = 1 \text{ kg m}^{-1} \text{ s}^{-1}$ ). In cgs system the unit of coefficient of viscosity is poise (named after great scientist Jean Louise Poiseuille).

$$1 \text{ poise} = 1 \text{ g cm}^{-1} \text{ s}^{-1} = 10^{-1} \text{ kg m}^{-1} \text{ s}^{-1}$$

Greater the viscosity, the more slowly the liquid flows. Hydrogen bonding and van der Waals forces are strong enough to cause high viscosity. Glass is an extremely viscous liquid. It is so viscous that many of its properties resemble solids. However, property of flow of glass can be experienced by measuring the thickness of windowpanes of old buildings. These become thicker at the bottom than at the top.

Viscosity of liquids decreases as the temperature rises because at high temperature molecules have high kinetic energy and can overcome the intermolecular forces to slip past one another between the layers.

## EXERCISE # S-I

- Calculate the pressure exerted by 22 g of carbon dioxide in  $0.5 \text{ dm}^3$  at 300 K using:
  - the ideal gas law and
  - Van der Waal's equation respectively.

**Given :**  $[a = 3.6 \text{ atm litre}^2 \text{ mol}^{-2}, b = 0.04 \text{ litre mol}^{-1}, R = 0.08 \text{ L-atm/K-mol}]$
- Calculate from the Van der Waals equation, the temperature at which 192 g of  $\text{SO}_2$  would occupy a volume of  $6 \text{ dm}^3$  at 15 atm pressure.  $[a = 5.68 \text{ atm L}^2 \text{ mol}^{-2}, b = 0.06 \text{ L mol}^{-1}]$
- The density of water vapour at 328.4 atm and 800 K is  $135.0 \text{ g/dm}^3$ . Determine the molar volume,  $V_m$  and the compression factor of water vapour.
- At 300 K and under a pressure of 10.1325 MPa, the compressibility factor of  $\text{O}_2$  is 0.9. Calculate the mass of  $\text{O}_2$  necessary to fill a gas cylinder of  $45 \text{ dm}^3$  capacity under the given conditions.  
 **$[R = 0.08 \text{ L-atm/K-mol}]$**
- 1 mole of  $\text{CCl}_4$  vapours at  $27^\circ\text{C}$  occupies a volume of 40 L. If Van der Waals constants are  $24.6 \text{ L}^2 \text{ atm mol}^{-2}$  and  $0.125 \text{ L mol}^{-1}$ , then, calculate compressibility factor in
  - Low pressure region
  - High Pressure region  $[R = 0.082 \text{ L -atm/K-mol}]$
- If at 200 K & 500 atm, density of  $\text{CH}_4$  is  $0.246 \text{ gm/ml}$  then its compressibility factor (Z) is approx  $2.0 \times 10^x$ . 'x' is:
- Certain mass of a gas occupy 500 ml at 2 atm and  $27^\circ\text{C}$ . Calculate the volume occupied by same mass of the gas at 0.3 atm and  $227^\circ\text{C}$ . The compressibility factors of gas at the given condition are 0.8 and 0.9, respectively.

## BOYLE TEMPERATURE

- The vander waal's constant for a gas are  $a = 1.92 \text{ atm L}^2 \text{ mol}^{-2}$ ,  $b = 0.06 \text{ L mol}^{-1}$ . If  $R = 0.08 \text{ L atm K}^{-1} \text{ mol}^{-1}$ , what is the Boyle's temperatrue of this gas.
- The Van der Waals constant for  $\text{O}_2$  are  $a = 1.642 \text{ atm L}^2 \text{ mol}^{-2}$  and  $b = 0.04 \text{ L mol}^{-1}$ . Calculate the temperature at which  $\text{O}_2$  gas behaves ideally for longer range of pressure.

## LIQUIFICATION OF GASES, CRITICAL PHENOMENON

- The Van der Waals constants for gases A, B and C are as follows

| Gas | $a[\text{atm L}^2 \text{ mol}^{-2}]$ | $b[\text{L mol}^{-1}]$ |
|-----|--------------------------------------|------------------------|
| A   | 8.21                                 | 0.050                  |
| B   | 4.105                                | 0.030                  |
| C   | 1.682                                | 0.040                  |

Which gas has (i) the highest critical temperature, (ii) the largest molecular volume, and (iii) most ideal behaviour around 500 K?

- For a real gas, if at critical conditions molar volume of gas is 8.21 litre at 3 atm, then critical temperature (in K) will be :
- An unknown gas behaves ideally at 540K in low pressure region, then calculate the temperature (in K) below which it can be liquified by applying pressure

## EXERCISE # S-II

1. The density of mercury is  $13.6 \text{ g/cm}^3$ . Estimate the value of 'b' (in  $\text{cm}^3/\text{mole}$ ).
2. The molarity of  $\text{O}_2$  gas at 72 atm and 300K is 6M. Calculate the value of Z for  $\text{O}_2$ .  
(Use :  $R = 0.08 \text{ atm-litre/K-mole}$ ).
3. Calculate the amount of He (in gm) present in the 10 litre container at 240 atm and 300K. Given value of "b" for He is  $0.08 \text{ dm}^3 \text{ mol}^{-1}$  ;  $R = 0.08 \text{ atm lit mol}^{-1} \text{ K}^{-1}$ .
4. For a real gas (mol. mass = 30) if density at critical point is  $0.40 \text{ g/cm}^3$  and its  $T_c = \frac{2 \times 10^5}{821} \text{ K}$ , then calculate Van der Waals constant a (in  $\text{atm L}^2 \text{mol}^{-2}$ ).
5. Calculate the volume occupied by 0.2 mole of a Vander waal gas at  $27^\circ\text{C}$  and 0.0821 atm.  
 $[a = 4.105 \text{ L}^2 \text{ atm mol}^{-2}, b = \frac{1}{6} \text{ Lmol}^{-1}]$
6. At what pressure and  $127^\circ\text{C}$ , the density of  $\text{O}_2$  gas becomes  $1.6 \text{ g/L}$  ?  
 $[a = 4.0 \text{ atm L}^2 \text{ mol}^{-2}, 0.4 \text{ Lmol}^{-1}, R = 0.08 \text{ L - atm/ K-mol}]$

## EXERCISE # O-1

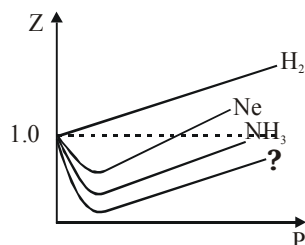
1. The correct expression for the Van der Waals equation of state is :

(A)  $\left(P + \frac{a}{n^2V^2}\right)(V - nb) = nRT$  (B)  $\left(P + \frac{an^2}{V^2}\right)(V - nb) = \Delta nRT$   
 (C)  $\left(P + \frac{an^2}{V^2}\right)(V - b) = nRT$  (D)  $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$

2. At relatively high pressure, Van der Waals equation reduces to :

(A)  $PV_m = RT$  (B)  $PV_m = RT + \frac{a}{V_m}$   
 (C)  $PV_m = RT + Pb$  (D)  $PV_m = RT - \frac{a}{V_m^2}$

3. Observe the following Z vs P graph.



The missing gas in the above graph can be :

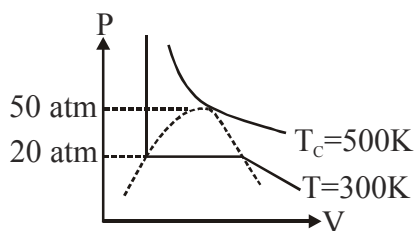
- (A) He (B) Ar (C)  $C_3H_{12}$  (D) All are correct
4. Correct option regarding a container containing 1 mol of a gas in 22.4 litre container at 273 K is  
 (A) If compressibility factor (Z) > 1 then 'P' will be less than 1 atm.  
 (B) If compressibility factor (Z) > 1 then 'P' will be greater than 1 atm.  
 (C) If 'b' dominates, pressure will be less than 1 atm.  
 (D) If 'a' dominates, pressure will be greater than 1 atm.
5. If 'V' is actual volume of 1 molecule of gas then, excluded volume (b) of 1 mole of gaseous molecule is -  
 (A)  $4 N_A V$  (B)  $N_A V$  (C)  $V/N_A$  (D) V
6. Consider the equation  $Z = \frac{PV}{RT}$ , Which of the following statements is correct :  
 (A) When  $Z > 1$  real gases are easier to compress  
 (B) When  $Z = 1$  real gases are easier to compress  
 (C) When  $Z > 1$  real gases are difficult to compress  
 (D) When  $Z < 1$  real gases are difficult to compress
7. Compressibility factor of ideal gas is :-  
 (A)  $z > 1$  (B)  $z > 1$  (C)  $z = 1$  (D)  $z = \infty$
8. The density of a gaseous substance at 1 atm pressure and 750 K is 0.30 g/lit. If the molecular weight of the substance is 27, the dominant forces existing among gas molecules is -  
 (A) Attractive (B) Repulsive  
 (C) Both (A) and (B) (D) None of these



9. The third virial coefficient of a He gas is  $4 \times 10^{-2} \text{ (lit/mol)}^2$ , then what will be volume of 2 mole He gas at 1 atm 273K ( $273\text{K} > T_B$ )  
 (A) 22.0 lit (B) 44.0 lit (C) 44.8 lit (D) 45.3 lit
10. At low pressure the vander waals equation is reduced to -  
 (A)  $Z = \frac{pV_m}{RT} = 1 - \frac{a}{RTV_m}$  (B)  $Z = \frac{pV_m}{RT} = 1 + \frac{a}{RT}p$   
 (C)  $pV_m = RT$  (D)  $Z = \frac{pV_m}{RT} = 1 - \frac{a}{RT}$
11. The values of Van der Waals constant 'a' for the gases  $O_2$ ,  $N_2$ ,  $NH_3$  and  $CH_4$  are 1.360, 1.390, 4.170 and 2.253 L atm mol<sup>-2</sup> respectively. The gas which can most easily be liquefied is :  
 (A)  $O_2$  (B)  $N_2$  (C)  $NH_3$  (D)  $CH_4$
12. The values of critical temperatures of few gases are given gases :  
**Gases :**  $H_2$     $He$     $O_2$     $N_2$   
 **$T_c(\text{K})$**    33.2   5.2   154.3   126  
 From the above data arrange the given gases in the increasing order of ease of their liquification.  
 (A)  $O_2$ ,  $N_2$ ,  $H_2$ ,  $He$  (B)  $He$ ,  $N_2$ ,  $O_2$ ,  $H_2$   
 (C)  $He$ ,  $H_2$ ,  $N_2$ ,  $O_2$  (D)  $H_2$ ,  $N_2$ ,  $O_2$ ,  $He$

## EXERCISE # O-II

1. For real gas the P-V curve was experimentally plotted and it had the following appearance. With respect to liquification, choose the incorrect statement :



- (A) At  $T = 500\text{ K}$ ,  $P = 40\text{ atm}$ , the state will be liquid  
 (B) At  $T = 300\text{ K}$ ,  $P = 50\text{ atm}$ , the state will be gas  
 (C) At  $T < 300\text{ K}$ ,  $P = 20\text{ atm}$ , the state will be gas  
 (D) At  $300\text{ K} < T < 500\text{ K}$ ,  $P > 50\text{ atm}$ , the state will be liquid
2. Select the incorrect statement (s)

(A) The critical constant for a Vander Waal's gas is  $V_c = 3b$ ,  $P_c = \frac{a}{27b^2}$  and  $T_c = \frac{a}{27Rb}$

(B) At  $56\text{ K}$  a gas may be liquified if its critical temperature is  $-156^\circ\text{C}$ .

(C)  $U_{\text{avg}}$  of gas in a rigid container can be doubled when the pressure is quadrupled by pumping in more gas at constant temperature

(D) At extremely low pressure, all real gases behave ideally.

3. A 1 litre vessel contains 2 moles of a vanderwaal's gas.

**Given data :**  $a = 2.5\text{ atm}\cdot\text{L}^2\text{ mole}^{-2}$   $T = 240\text{ K}$

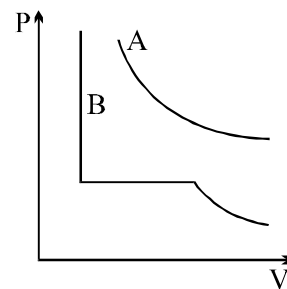
$$b = 0.4\text{ L}\cdot\text{mole}^{-1} \quad RT = 20\text{ L}\cdot\text{atm mole}^{-1}$$

Identify the correct options about the gas sample :

- (A) Pressure of gas =  $190\text{ atm}$   
 (B) Compressibility factor =  $4.75$   
 (C) Attraction forces are dominant in the gaseous sample  
 (D)  $T_B$  (Boyle temperature) =  $75\text{ K}$
4. Choose the correct statement(s) among the following -
- (A) A gas having higher value  $T_c$  is easy to liquify  
 (B) The radius of molecules of gas having same value of  $T_c/P_c$  is same  
 (C) Hydrogen gas can be liquified at its boyle temperature by application of pressure.  
 (D) Real gas show negative deviation from ideal behaviour at low pressure condition.
5. Select the INCORRECT statement(s):
- (A) At Boyle's temperature a real gas behaves like an ideal gas irrespective of pressure.  
 (B) At critical condition, a real gas behaves like an ideal gas.  
 (C) On increasing the temperature four times, collision frequency ( $Z_1$ ) becomes double at constant volume.  
 (D) At high pressure Van der Waals constant 'b' dominates over 'a'.

Question No. 6 & 7 (2 questions)

For two gases A and B, P v/s V isotherms are shown at same temperature, T K.  $T_A$  &  $T_B$  are critical temperatures of A & B respectively



6. Which of the following is true?

- (A)  $T_A < T < T_B$       (B)  $T_A > T > T_B$   
 (C)  $T_A > T_B > T$       (D) none of above

7. The correct statement(s) is/are

- (I) Pressure correction term will be more negligible for gas B at T K.  
 (II) The curve for gas 'B' will be of same shape as for gas A if  $T > T_B$   
 (III) Gas 'A' will show same P v/s V curve as of gas 'B' if  $T > T_A$

- (A) III only      (B) II and III      (C) II only      (D) All

Match the column :

8. Match the column :

Column-I

- (A) Boyle's temperature  
 (B) Compressibility factor  
 (C) Real gas with very large molar volume  
 (D) Critical temperature

Column-II

- (P) Depends on 'a' and 'b'  
 (Q) Depends on identity of real gas  
 (R) The temperature at which  $\frac{dZ}{dP} = 0$  at low pressure region.  
 (S)  $PV = nRT$   
 (T)  $\frac{8a}{27R.b.}$

## EXERCISE # JEE-MAINS

1. In Van der Waals equation of state of the gas law, the constant 'b' is a measure of: [AIEEE-04]  
(1) intermolecular repulsions  
(2) intermolecular attractions  
(3) volume occupied by the molecules  
(4) intermolecular collisions per unit volume
2. 'a' and 'b' are Van der Waals constants for gases. Chlorine is more easily liquefied than ethane because :- [AIEEE-2011]  
(1)  $a$  for  $\text{Cl}_2 < a$  for  $\text{C}_2\text{H}_6$  but  $b$  for  $\text{Cl}_2 > b$  for  $\text{C}_2\text{H}_6$   
(2)  $a$  for  $\text{Cl}_2 > a$  for  $\text{C}_2\text{H}_6$  but  $b$  for  $\text{Cl}_2 < b$  for  $\text{C}_2\text{H}_6$   
(3)  $a$  and  $b$  for  $\text{Cl}_2 > a$  and  $b$  for  $\text{C}_2\text{H}_6$   
(4)  $a$  and  $b$  for  $\text{Cl}_2 < a$  and  $b$  for  $\text{C}_2\text{H}_6$
3. When does a gas deviate the most from its ideal behaviour? [JEE-MAINS(ONLINE)-2015]  
(1) At high pressure and low temperature  
(2) At high pressure and high temperature  
(3) At low pressure and low temperature  
(4) At low pressure and high temperature
4. If  $Z$  is the compressibility factor, Van der Waals equation at low pressure can be written as : [JEE-MAINS-2014]  
(1)  $Z = 1 - \frac{Pb}{RT}$       (2)  $Z = 1 + \frac{Pb}{RT}$       (3)  $Z = 1 + \frac{RT}{Pb}$       (4)  $Z = 1 - \frac{a}{V_m RT}$
5. Among the following, the incorrect statement is : [JEE-Mains-2017(ONLINE)]  
(1) At low pressure, real gases show ideal behaviour  
(2) At very large volume, real gases show ideal behaviour  
(3) At Boyle's temperature, real gases show ideal behaviour  
(4) At very low temperature, real gases show ideal behaviour

EXERCISE # JEE-ADVANCED

1. One way of writing the equation of state for real gases is, [JEE 1997]

$$P \bar{V} = RT \left[ 1 + \frac{B}{\bar{V}} + \dots \right] \quad \text{where } B \text{ is a constant.}$$

Derive an approximate expression for 'B' in terms of Van der Waals constants 'a' & 'b'.

2. Using Vander Waals equation, calculate the constant "a" when 2 moles of a gas confined in a 4 litre flask exerts a pressure of 11.0 atm at a temperature of 300 K. The value of "b" is 0.05 litre mol<sup>-1</sup>.
3. A gas will approach ideal behaviour at : [JEE 1999]  
 (A) low temperature and low pressure  
 (B) low temperature and high pressure  
 (C) low pressure and high temperature  
 (D) high temperature and high pressure .
4. The compression factor (compressibility factor) for one mole of a Van der Waals gas at 0°C and 100 atmosphere pressure is found to be 0.5. Assuming that the volume of a gas molecule is negligible, calculate the Van der Waals constant 'a'. [JEE 2001]
5. The density of the vapour of a substance at 1 atm pressure and 500 K is 0.36 Kg m<sup>-3</sup>. The vapour effuses through a small hole at a rate of 1.33 times faster than oxygen under the same condition.

Determine

[JEE 2002]

- (i) mol. wt.; (ii) molar volume ; (iii) compression factor (z) of the vapour and  
 (iv) which forces among the gas molecules are dominating, the attractive or the repulsive

6. Positive deviation from ideal behaviour takes place because of [JEE 2003]

(A) molecular attraction between atoms and  $\frac{PV}{nRT} > 1$

(B) molecular attraction between atoms and  $\frac{PV}{nRT} < 1$

(C) finite size of atoms and  $\frac{PV}{nRT} > 1$

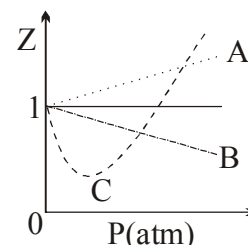
(D) finite size of atoms and  $\frac{PV}{nRT} < 1$

7. For a real gas obeying Van der Waals equation a graph is plotted between  $PV_m$  (y-axis) and  $P$  (x-axis) where  $V_m$  is molar volume. Find y-intercept of the graph. [JEE 2004]

8. The given graph represents the variation of Z

(compressibility factor =  $\frac{PV}{nRT}$ ) versus P, for three real

gases A, B and C. Identify the only **INCORRECT** statement.



- (A) for the gas A,  $a = 0$  and its dependence on P is linear at all pressure  
 (B) for the gas B,  $b = 0$  and its dependence on P is linear at all pressure  
 (C) for the gas C, which is typical real gas for which neither a nor b = 0. By knowing the minima and the point of intersection, with  $Z = 1$ , a and b can be calculated.  
 (D) At high pressure, the slope is positive for all real gases A, B and C. [JEE 2006]



# ANSWER KEY

## EXERCISE # S-I

- |                                        |                            |
|----------------------------------------|----------------------------|
| 1. (a) 24.0 atm, (b) 21.4 atm          | 2. 388K                    |
| 3. Molar vol = 0.1333 L/mol; Z = 0.667 | 4. 6.67 kg                 |
| 5. (a) 0.975; (b) 1.003                | 6. Ans. (0)                |
| 7. 6.25 L                              | 8. Ans. (400K)             |
| 9. 500 K                               | 10. (i) A, (ii) A, (iii) C |
| 11. Ans. (800)                         | 12. Ans. (160K)            |

## EXERCISE # S-II

- |                  |               |
|------------------|---------------|
| 1. 58.82         | 2. Ans.(0.5)  |
| 3. Ans. (222.22) | 4. 1.6875     |
| 5. 6L            | 6. 1.622 atm. |

## EXERCISE # O-I

- |             |              |              |             |
|-------------|--------------|--------------|-------------|
| 1. Ans. (D) | 2. Ans.(C)   | 3. Ans.(C)   | 4. Ans.(B)  |
| 5. Ans. (A) | 6. Ans.(C)   | 7. Ans.(C)   | 8. Ans.(B)  |
| 9. Ans. (D) | 10. Ans. (A) | 11. Ans. (D) | 12. Ans.(C) |

## EXERCISE # O-II

- |                                                             |              |                |                |
|-------------------------------------------------------------|--------------|----------------|----------------|
| 1. Ans.(A,B,C)                                              | 2. Ans.(A,C) | 3. Ans.(A,B,D) | 4. Ans.(A,B,D) |
| 5. Ans.(A,B)                                                | 6. Ans.(A)   | 7. Ans.(C)     |                |
| 8. Ans.(A) - P,Q,R,S ; (B) - P, Q ; (C) - S ; (D) - P, Q, T |              |                |                |

## EXERCISE # JEE-MAINS

- |             |             |             |             |
|-------------|-------------|-------------|-------------|
| 1. Ans.(3)  | 2. Ans. (2) | 3. Ans. (1) | 4. Ans. (4) |
| 5. Ans. (4) |             |             |             |

## EXERCISE # JEE-ADVANCED

- |                                                                                |                                                    |
|--------------------------------------------------------------------------------|----------------------------------------------------|
| 1. $\left[ B = b - \frac{a}{RT} \right]$                                       | 2. 6.52 atm L <sup>2</sup> mol <sup>-2</sup>       |
| 3. Ans. (C)                                                                    | 4. Ans. 1.256 atm L <sup>2</sup> mol <sup>-2</sup> |
| 5. Ans.(i) 18 g/mol, (ii) 50 L mol <sup>-1</sup> , (iii) 1.218, (iv) repulsive |                                                    |
| 6. Ans.(C)                                                                     | 7. Ans.RT                                          |
| 8. Ans.(D)                                                                     | 9. Ans.(A) P, S; (B) R; (C) P, Q; (D) R            |
| 10. Ans.(A,C,D)                                                                | 11. Ans.(B)                                        |
| 12. Ans.(C)                                                                    |                                                    |

## LIQUID SOLUTION

### 1. SOLUTION

It is the homogeneous mixture of two or more components.

The substance which dissolve other substance is **solvent** & the substance which is dissolved is **solute**, independent of their quantity. If both are soluble in each other then the substance present in larger amount by mole is solvent.

\* A solution may exist in any physical state.

#### Types of Solution :

|    | Solvent | Solute | Examples                                                         |
|----|---------|--------|------------------------------------------------------------------|
| 1. | Gas     | Gas    | Mixture of gases, eg. air.                                       |
| 2. | Gas     | Liquid | $\text{CHCl}_3(\ell) + \text{N}_2(\text{g})$                     |
| 3. | Gas     | Solid  | Camphor (s) + $\text{N}_2(\text{g})$ .                           |
| 4. | Liquid  | Gas    | $\text{CO}_2$ gas dissolve in water (aerated drink), soda water. |
| 5. | Liquid  | Liquid | Mixture of miscible liquids e.g. alcohol in water.               |
| 6. | Liquid  | Solid  | Salt in water, sugar in water.                                   |
| 7. | Solid   | Gas    | hydrogen over palladium.                                         |
| 8. | Solid   | Liquid | Mercury in zinc, mercury in gold, i.e. all amalgams.             |
| 9. | Solid   | Solid  | Alloys e.g. copper in gold, zinc in copper.                      |

### 2. SOLUBILITY

Maximum amount of solute which can be dissolved in a specified amount of solvent at constant temperature is to solubility. Solubility is affected by

1. nature of solute and solvent
2. temperature and
3. pressure

### 3. SOLUBILITY OF SOLID IN A LIQUID

Polar solutes are soluble in polar solvent and non polar solutes are soluble in non polar solvent due to similar intermolecular forces.

When solid solutes are dissolved in solvent, then following equilibrium exists.

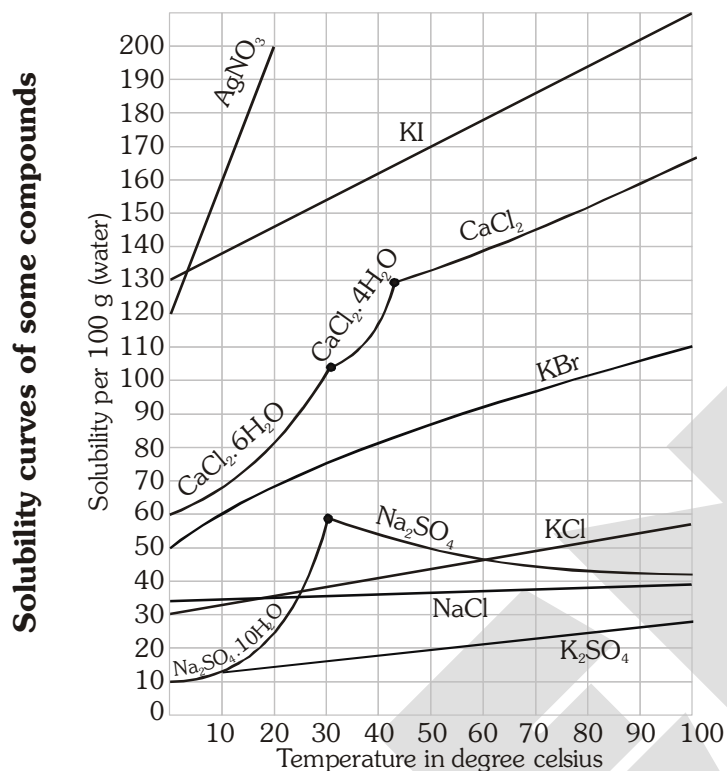
Solute + Solvent  $\xrightleftharpoons[\text{Crystallization}]{\text{Dissolution}}$  Solution. ;  $\Delta H$  may be positive or negative

Such a solution in which no more solute can be dissolved at the same temperature and pressure is called a **saturated solution**. An unsaturated solution is one in which more solute can be dissolved at the same temperature. The solution which is in dynamic equilibrium with undissolved solute is the saturated solution and contains the maximum amount of solute dissolved in a given amount of solvent.

#### 3.1 Effect of temperature :

The solubility of a solid in a liquid is significantly affected by temperature changes, obeying **Le Chateliers Principle**. In general, if in a nearly saturated solution, the dissolution process is endothermic ( $\Delta_{\text{sol}}H > 0$ ), the solubility should increase with rise in temperature and if it is exothermic ( $\Delta_{\text{sol}}H < 0$ ) the solubility should decrease. These trends are also observed experimentally.





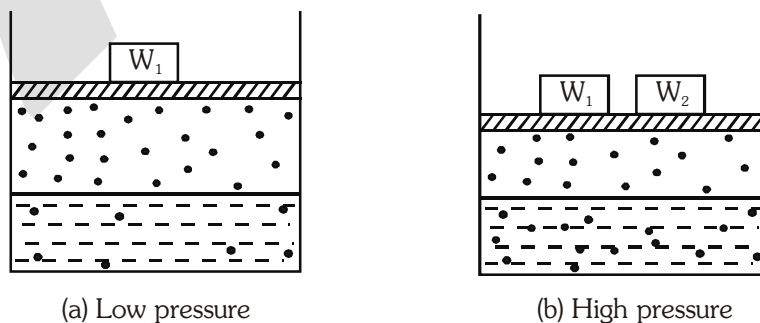
### 3.2 Effect of pressure :

Pressure does not have any significant effect on solubility of solids in liquids. It is so because solids and liquids are highly incompressible and practically remain unaffected by changes in pressure.

## 4. SOLUBILITY OF GASES IN LIQUID

Certain gases are highly soluble in water like  $\text{NH}_3$ ,  $\text{HCl}$ , etc, and certain gases are less soluble in water like  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{He}$ , etc. Solubility of gases is greatly effected by pressure and temperature. Increasing pressure increases solubility and increase in temperature decreases solubility since dissolution of any gas in any liquid is exothermic in nature.

### 4.1 Henry' Law :



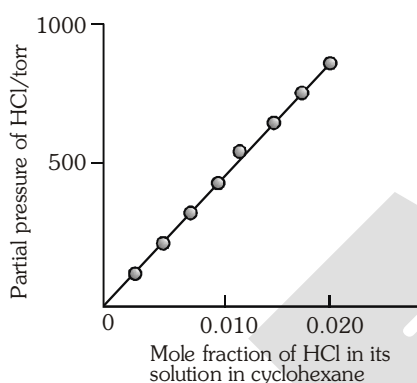
*Effect of pressure on the solubility of a gas. The concentration of dissolved gas is proportional to the pressure on the gas above the solution.*

The partial pressure of the gas in vapour phase ( $p$ ) is proportional to the mole fraction of the gas ( $x$ ) in the solution, at constant temperature

$$P = K_H X$$

$K_H$  = Henry's Law Constant

- \* Henry's Law Constant depends on nature of gas and liquid as well as temperature.
- \*  $K_H$  increases with increases in temperature.
- \* Greater  $K_H$  means low solubility.



Experimental results for the solubility of HCl gas in cyclohexane at 293 K. The slope of the line is the Henry's Law constant  $K_H$

**Values of Henry's Law Constant for Some Selected Gases in Water**

| Gas             | Temperature/K | $K_H$ /kbar           |
|-----------------|---------------|-----------------------|
| He              | 293           | 144.97                |
| H <sub>2</sub>  | 293           | 69.16                 |
| N <sub>2</sub>  | 293           | 76.48                 |
| N <sub>2</sub>  | 303           | 88.84                 |
| O <sub>2</sub>  | 293           | 34.86                 |
| O <sub>2</sub>  | 303           | 46.82                 |
| Argon           | 298           | 40.3                  |
| CO <sub>2</sub> | 298           | 1.67                  |
| Formaldehyde    | 298           | $1.83 \times 10^{-5}$ |
| Methane         | 298           | 0.413                 |
| Vinyl chloride  | 298           | 0.611                 |

## 4.2 Limitations of Henry's Law :

- (1) It is valid only for ideal behaviour of gas. As none of the gas is ideal, this law may be applied at low pressure and high temperature.
- (2) It gives better result when the solubility of gas in the liquid is low.
- (3) The gas should neither dissociate nor associate in the liquid.

### 4.3 Henry' Law application :

- (1) To increase the solubility of  $\text{CO}_2$  in soft drinks and soda water, the bottle is sealed under high pressure.
- (2) Scuba divers must cope with high concentrations of dissolved gases while breathing air at high pressure underwater. Increased pressure increases the solubility of atmospheric gases in blood. When the divers come towards surface, the pressure gradually decreases. This releases the dissolved gases and leads to the formation of bubbles of nitrogen in the blood. This blocks capillaries and creates a medical condition known as bends, which are painful and dangerous to life. To avoid bends, as well as, the toxic effects of high concentrations of nitrogen in the blood, the tanks used by scuba divers are filled with air diluted with helium (11.7% helium, 56.2% nitrogen and 32.1% oxygen).
- (3) At high altitudes the partial pressure of oxygen is less than that at the ground level. This leads to low concentrations of oxygen in the blood and tissues of people living at high altitudes or climbers. Low blood oxygen causes climbers to become weak and unable to think clearly, symptoms of a condition known as anoxia.

### 4.4 Effect of Temperature :

Solubility of any gas in any liquid decreases with rise in temperature as dissolution is an exothermic process.

At constant pressure, 
$$\ln \frac{C_2}{C_1} = \frac{\Delta H_{\text{sol}}}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

where C = molar concentration of gas in solution

**Ex.1.** If  $\text{N}_2$  gas is bubbled through water at 293 K, how many millimoles of  $\text{N}_2$  gas would dissolve in 1 litre of water? Assume that  $\text{N}_2$  exerts a partial pressure of 0.987 bar. Given that Henry's law constant for  $\text{N}_2$  at 293 K is 76.48 kbar.

**Sol:** 
$$x(\text{Nitrogen}) = \frac{p(\text{nitrogen})}{K_H} = \frac{0.98 \text{ bar}}{76,480 \text{ bar}} = 1.29 \times 10^{-5}$$

As 1 litre of water contains 55.5 mol of it, therefore if  $n$  represents number of moles of  $\text{N}_2$  in solution,

$$x(\text{Nitrogen}) = \frac{n \text{ mol}}{n \text{ mol} + 55.5 \text{ mol}} = \frac{n}{55.5} = 1.29 \times 10^{-5}$$

( $n$  in denominator is neglected as it is  $\ll 55.5$ )

$$\text{Thus } n = 1.29 \times 10^{-5} \times 55.5 \text{ mol} = 7.16 \times 10^{-4} \text{ mol} = 0.716 \text{ m mol}$$

**Ex.2** The air is a mixture of a number of gases. The major components are oxygen and nitrogen with approximate proportion of 20% is to 79% by volume at 298 K. The water is in equilibrium with air at a pressure of 10 atm. At 298 K, if the Henry's law constants for oxygen and nitrogen are  $3.30 \times 10^7 \text{ mm}$  and  $6.51 \times 10^7 \text{ mm}$  respectively, calculate the composition of these gases in water.

**Sol:** Percentage of oxygen ( $\text{O}_2$ ) in air = 20%

Percentage of nitrogen ( $\text{N}_2$ ) in air = 79%

Also, it is given that water is in equilibrium with air at a total pressure of 10 atm, that is,  $(10 \times 760) \text{ mm Hg} = 7600 \text{ mm Hg}$

$$\text{Partial pressure of oxygen, } p_{\text{O}_2} = \frac{20}{100} \times 7600 \text{ mm Hg} = 1520 \text{ mm Hg}$$

Partial pressure of nitrogen,  $p_{N_2} = \frac{79}{100} \times 7600 \text{ mm Hg} = 6004 \text{ mm of Hg}$

Now, according to Henry's law :

$$p = K_H x$$

For oxygen :

$$p_{O_2} = K_H \cdot x_{O_2}$$

$$\Rightarrow x_{O_2} = \frac{p_{O_2}}{K_H} = \frac{1520 \text{ mm of Hg}}{3.30 \times 10^7 \text{ mm of Hg}} \quad (\text{Given } K_H = 3.30 \times 10^7 \text{ mm of Hg} = 4.61 \times 10^{-5})$$

For nitrogen,

$$p_{N_2} = K_H \cdot x_{N_2}$$

$$\Rightarrow x_{N_2} = \frac{p_{N_2}}{K_H} = \frac{6004 \text{ mm Hg}}{6.51 \times 10^7 \text{ mm Hg}} = 9.22 \times 10^{-5}$$

Hence, the mole fractions of oxygen and nitrogen in water are  $4.61 \times 10^{-5}$  and  $9.22 \times 10^{-5}$  respectively.

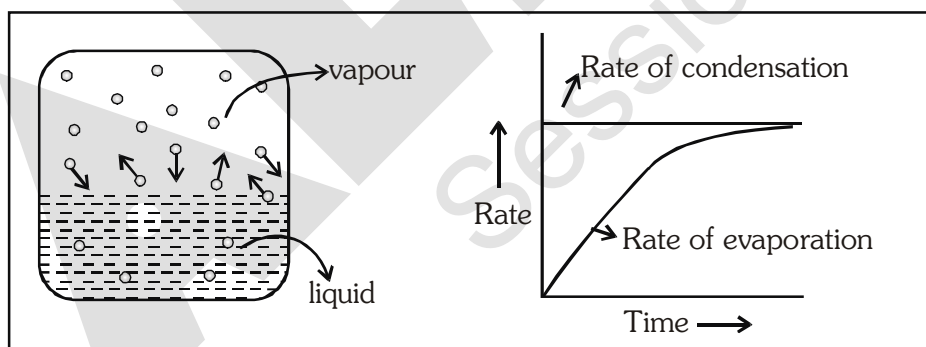
## 5. Vapour pressure :

### The Evaporation of a Liquid in a Closed Container

When a liquid is taken in a closed vessel at constant temperature, then there are two process which takes place.

- (i) evaporation                      (ii) condensation

In the constant evaporation from the surface particles continue to break away from the surface of the liquid. As the gaseous particles bounce around, some of them will hit the surface of the liquid again, and will be trapped there. This is called condensation. The rate of condensation increases with time, but rate of evaporation remain constant. There will rapidly be an equilibrium set up in which the number of particles leaving the surface is exactly balanced by the number rejoining it.



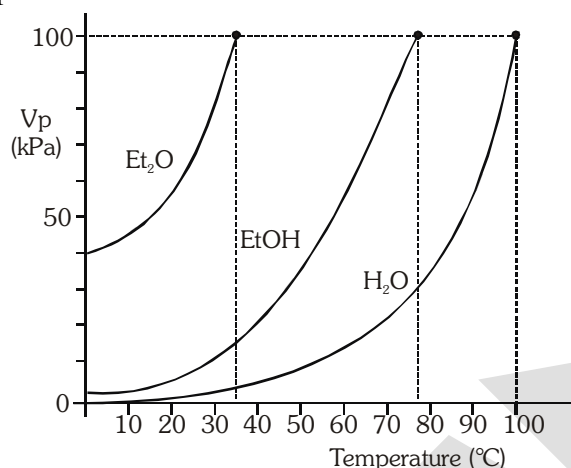
This pressure at equilibrium is called the **vapour pressure** (also known as **saturation vapour pressure**) of the liquid at that temperature.

### 5.1 Effect of Temperature on vapour pressure

When the space above the liquid is saturated with vapour particles, you have this equilibrium occurring on the surface of the liquid :



The forward change (liquid to vapour) is endothermic. It needs heat to convert the liquid into the vapour. According to Le Chatelier, increasing the temperature of a system in a dynamic equilibrium favours the endothermic change. That means increasing the temperature increase the amount of vapour present, and so increases the vapour pressure.



**Effect of nature :**  $V.p \propto \frac{1}{\text{Inter molecular attraction force(I.M.A.F.)}}$



The dependence of vapour pressure of a liquid on temperature is given by clausius-clapeyron

$$\text{equation : } \ln \frac{P_2}{P_1} = \frac{\Delta H_{\text{vap.}}}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

**5.2 Nature of liquid :** Weaker the intermolecular attraction, higher will be the vapour pressure.

## 6. VAPOUR PRESSURE OF LIQUID SOLUTION

### 6.1 Raoult's law :

The partial pressure of any volatile constituents of a solution at a constant temperature is equal to the vapour pressure of pure constituents multiplied by the mole fraction of that constituent in the solution, at equilibrium.

### 6.2 Vapour pressure of liquid – liquid solution :

Let  $P_A$  and  $P_B$  be the partial vapour pressures of two constituents A and B in solution and  $P_A^0$  and  $P_B^0$  the vapour pressures in pure state respectively.

Thus, according Raoult's law

$$P_A = \frac{n_A}{n_A + n_B} P_A^0 = X_A P_A^0 \quad \dots(1)$$

$$\text{and } P_B = \frac{n_B}{n_A + n_B} P_B^0 = X_B P_B^0 \quad \dots(2)$$

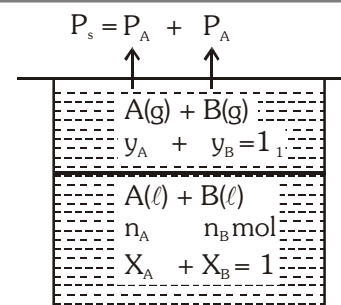
If total pressure be  $P_s$ , then

$$P_s = P_A + P_B = X_A P_A^0 + X_B P_B^0$$

$$P_s = X_A P_A^0 + (1 - X_A) P_B^0 \quad [\because X_A + X_B = 1]$$

$$P_s = X_A P_A^0 - X_A P_B^0 + P_B^0$$

$$P_s = X_A [P_A^0 - P_B^0] + P_B^0$$



### 6.2.1 Relation between Dalton's Law and Raoult's Law :

The composition of the vapour in equilibrium with the solution can be calculated applying Dalton's law of partial pressures. Let the mole fraction of A and B in vapours be  $Y_A$  and  $Y_B$  respectively.

$$p_A = Y_A P_s = X_A P_A^0 \quad \text{.....(1)}$$

$$p_B = Y_B P_s = X_B P_B^0 \quad \text{.....(2)}$$

Now,  $X_A = \frac{Y_A \cdot P_s}{P_A^0}$  and  $X_B = \frac{Y_B \cdot P_s}{P_B^0}$

As,  $X_A + X_B = 1$ ,  $\frac{Y_A \cdot P_s}{P_A^0} + \frac{Y_B \cdot P_s}{P_B^0} = 1$

$$\therefore \frac{1}{P_s} = \frac{Y_A}{P_A^0} = \frac{Y_B}{P_B^0}$$

Hence, the total vapour pressure of solution may be calculated from liquid composition at equilibrium as

$$P_s = X_A \cdot P_A^0 + X_B \cdot P_B^0$$

and from vapour composition at equilibrium at

$$\frac{1}{P_s} = \frac{Y_A}{P_A^0} + \frac{Y_B}{P_B^0}$$

### 6.2.2 Comparison between liquid and vapour composition :

$$\frac{Y_A}{Y_B} = \frac{P_A / P_s}{P_B / P_s} = \frac{P_A}{P_B} = \frac{X_A \cdot P_A^0}{X_B \cdot P_B^0}$$

If A is more volatile than B ( $P_A^0 > P_B^0$ ), then  $\frac{Y_A}{Y_B} > \frac{X_A}{X_B}$

It means that the mole-fraction of A in vapour form is relatively greater than that in liquid form, relative to B. Hence, in any ideal solution, vapour is always more richer in the more volatile component.

### 6.2.3 Raoult's law as a special case of Henry's law :

From Raoult's law, the vapour pressure of volatile component in the solution is  $P = P^0 \cdot X$ .

In the solution of gas in liquid, one component is so volatile that it exists as gas and its pressure is given by Henry's law as  $P = K_H \cdot X$

In both laws, the partial pressure of volatile component is directly proportional to its mole-fraction in solution. Only the proportionality constant  $K_H$  differs from  $P^0$ . Hence, Raoult's law becomes a special case of Henry's law in which  $K_H$  becomes  $P^0$ .

### 6.3 Vapour pressure of solution of solids in liquid :

Let us assume A = non volatile solid & B = volatile liquid

According to Raoult's law –

$$\therefore P_s = X_A P_A^0 + X_B P_B^0$$

for A,  $P_A^0 = 0$

$$\therefore P_s = X_B P_B^0 \quad \dots(5)$$

Let  $P_B^0 = P^0$  = Vapour pressure of pure state of solvent.

here  $X_B$  is mole fraction of solvent

$$P_s = \frac{n_B}{n_A + n_B} P^0 \quad \dots(6)$$

$$P_s \propto \frac{n_B}{n_A + n_B} \quad \text{i.e. vapour pressure of solution} \propto \text{mole fraction of solvent}$$

$$\Rightarrow P_s = X_B P_B^0 \Rightarrow P_s = (1 - X_A) P_B^0$$

$$\Rightarrow P_s = P_B^0 - X_A P_B^0$$

$$\Rightarrow \frac{P_B^0 - P_s}{P_B^0} = X_A$$

$$\text{or } \frac{P^0 - P_s}{P^0} = X_A \quad \dots(7)$$

$$\boxed{\frac{P^0 - P_s}{P^0} = \frac{n_A}{n_A + n_B}} \quad \dots(8)$$

$$\text{or } \frac{P^0}{P^0 - P_s} = \frac{n_A + n_B}{n_A}$$

$$\text{or } \frac{P^0}{P^0 - P_s} = 1 + \frac{n_B}{n_A} \quad \text{or } \frac{P^0}{P^0 - P_s} - 1 = \frac{n_B}{n_A}$$

$$\frac{P_s}{P^0 - P_s} = \frac{n_B}{n_A}$$

$$\boxed{\frac{P^0 - P_s}{P_s} = \frac{n_A}{n_B} = \frac{w_A \cdot m_B}{m_A \cdot w_B}} \quad \dots(9)$$

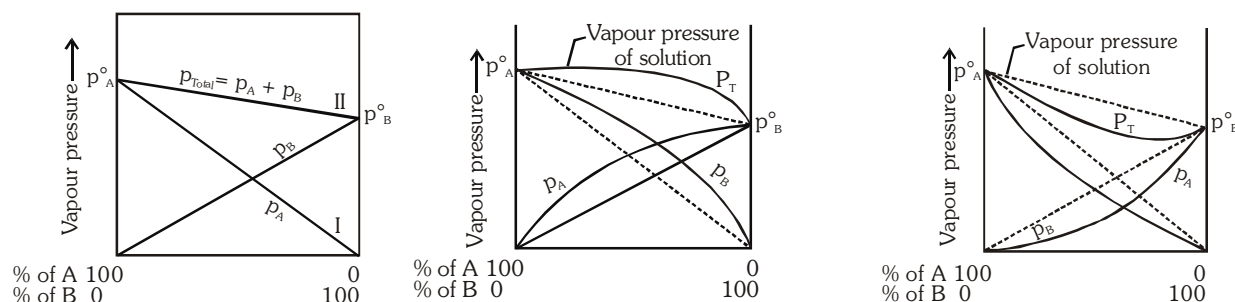
### 6.4 Ideal and Non ideal solutions :

The solutions which obey Raoult's law over the entire range of concentration are known as ideal solutions.

**Table : Comparison between Ideal and Non-ideal solutions**

| Ideal solutions                                                                                                                                                                                                                                                                                                                                                                 | Non-ideal solutions                                                                                                                                                                                                                                                               |                                                                                                                                                                                                                                                                 |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|                                                                                                                                                                                                                                                                                                                                                                                 | +ve deviation from Raoult's law                                                                                                                                                                                                                                                   | - deviation from Raoult's law                                                                                                                                                                                                                                   |
| 1. Obeys Raoult's law at every concentrations.                                                                                                                                                                                                                                                                                                                                  | Do not obey Raoult's law.                                                                                                                                                                                                                                                         | Do not obey Raoult's law.                                                                                                                                                                                                                                       |
| 2. $\Delta H_{\text{mix}} = 0$ ; Neither heat is evolved nor absorbed during dissolution.                                                                                                                                                                                                                                                                                       | $\Delta H_{\text{mix}} > 0$ . Endothermic dissolution; heat is absorbed.                                                                                                                                                                                                          | $\Delta H_{\text{mix}} < 0$ ; exothermic dissolution heat is evolved.                                                                                                                                                                                           |
| 3. $\Delta V_{\text{mix}} = 0$ ; total volume of solution is equal to sum of volumes of the components.                                                                                                                                                                                                                                                                         | $\Delta V_{\text{mix}} > 0$ . Volume is increased after dissolution.                                                                                                                                                                                                              | $\Delta V_{\text{mix}} < 0$ ; volume is decreased during dissolution.                                                                                                                                                                                           |
| 4. $P = p_A + p_B = p_A^0 X_A + p_B^0 X_B$<br>i.e., $P_A = p_A^0 X_A$ ; $p_B = p_B^0 X_B$                                                                                                                                                                                                                                                                                       | $P_A > p_A^0 X_A$ ; $p_B > p_B^0 X_B$<br>$\therefore (P_A + p_B) > (p_A^0 X_A + p_B^0 X_B)$                                                                                                                                                                                       | $P_A < p_A^0 X_A$ ; $p_B < p_B^0 X_B$<br>$\therefore (P_A + p_B) < (p_A^0 X_A + p_B^0 X_B)$                                                                                                                                                                     |
| 5. A—A, A—B, B—B interactions should be same, i.e., 'A' and 'B' are identical in shape, size and character.                                                                                                                                                                                                                                                                     | A—B, attraction force should be weaker than A—A and B—B attractive forces. 'A' and 'B' have different shape, size and character.                                                                                                                                                  | A—B, attraction force should be greater than A—A and B—B attractive forces. 'A' and 'B' have different shape, size and character.                                                                                                                               |
| 6. Escaping tendency of 'A' and 'B' should be same in pure liquids and in the solution.                                                                                                                                                                                                                                                                                         | 'A' and 'B' escape easily showing high vapour pressure than the expected value.                                                                                                                                                                                                   | Escaping tendency of both components A and B is lowered showing lower vapour pressure than expected ideally.                                                                                                                                                    |
| <b>Example :</b><br>dilute solutions ;<br>benzene + toluene ;<br>n-hexane + n-heptane ;<br>chlorobenzene + bromobenzene ;<br>ethyl bromide + ethyl iodide ;<br>n-butyl chloride + n-butyl bromide<br>$\text{CCl}_4 + \text{SiCl}_4$ ;<br>$\text{C}_2\text{H}_4\text{Br}_2 + \text{C}_2\text{H}_4\text{Cl}_2$<br>$\text{C}_2\text{H}_5\text{Br} + \text{C}_2\text{H}_5\text{Cl}$ | <b>Example :</b><br>acetone + ethanol ;<br>acetone + $\text{CS}_2$ ;<br>water + methanol ;<br>water + ethanol ;<br>$\text{CCl}_4 + \text{CHCl}_3$ ;<br>$\text{CCl}_4 + \text{toluene}$ ;<br>acetone + benzene<br>$\text{CCl}_4 + \text{CH}_3\text{OH}$ ;<br>cyclohexane + ethanol | <b>Example :</b><br>acetone + aniline ;<br>acetone + chloroform ;<br>$\text{CH}_3\text{OH} + \text{CH}_3\text{COOH}$ ;<br>$\text{H}_2\text{O} + \text{HNO}_3$ ;<br><br>water + $\text{HCl}$ ;<br>acetic acid + pyridine ;<br><br>$\text{HNO}_3 + \text{CHCl}_3$ |





**Ex.3.** 1 mole heptane (V.P. = 92 mm of Hg) is mixed with 4 mole Octane (V.P. = 31 mm of Hg), form an ideal solution. Find out the vapour pressure of solution.

**Sol.** Total mole = 1 + 4 = 5

Mole fraction of heptane =  $X_A = 1/5$

Mole fraction of octane =  $X_B = 4/5$

$$P_s = X_A P_A^0 + X_B P_B^0 = \frac{1}{5} \times 92 + \frac{4}{5} \times 31 = 43.2 \text{ mm of Hg.}$$

**Ex.4.** At 88°C, benzene has a vapour pressure of 900 torr and toluene has a vapour pressure of 360 torr. What is the mole fraction of benzene in the mixture with toluene that will be boil at 88°C at 1 atm pressure, benzene – toluene form an ideal solution.

**Sol.**  $P_s = 760$  torr, because solution boils at 88°C

$$\therefore 760 = 900x + 360(1-x)$$

$$x = 0.74 \text{ where 'x' is mole fraction } C_6H_6.$$

**Ex.5.** The vapour pressure of benzene at 90°C is 1020 torr. A solution of 5 g of a solute in 58.5 g benzene has vapour pressure 990 torr. What is the molecular weight of solute ?

$$\text{Sol. } \frac{P^0 - P_s}{P_s} = \frac{w \times M}{m \times W} \Rightarrow \frac{1020 - 990}{990} = \frac{5 \times 78}{m \times 58.5} \Rightarrow m = 220$$

**Ex.6.** Two liquids A and B form an ideal solution. At 300 K, the vapour pressure of a solution containing 1 mole of A and 3 mole of B is 550 mm of Hg. At the same temperature, if one more mole of B is added to this solution, the vapour pressure of the solution increases by 10 mm of Hg. Determine the vapour pressure of A and B in their pure states.

**Sol.** Let the vapour pressure of pure A be =  $p_A^0$ ; and the vapour pressure of pure B be =  $p_B^0$ .

Total vapour pressure of solution (1 mole A + 3 mole B)

$$= X_A \cdot p_A^0 + X_B \cdot p_B^0 \quad [X_A \text{ is mole fraction of A and } X_B \text{ is mole fraction of B}]$$

$$550 = \frac{1}{4} p_A^0 + \frac{3}{4} p_B^0 \quad \text{or} \quad 2200 = p_A^0 + 3p_B^0 \quad \dots\dots(i)$$

$$\text{Total vapour pressure of solution (1 mole A + 4 mole B)} = \frac{1}{5} p_A^0 + \frac{4}{5} p_B^0$$

$$560 = \frac{1}{5} p_A^0 + \frac{4}{5} p_B^0$$

$$2800 = p_A^0 + p_B^0 \quad \dots\dots(ii)$$

Solving eqs. (i) and (ii)

$$p_B^0 = 600 \text{ mm of Hg} = \text{vapour pressure of pure B}$$

$$p_A^0 = 400 \text{ mm of Hg} = \text{vapour pressure of pure A}$$

**Ex.7.** Liquids 'A' and 'B' form an ideal solution. Calculate the vapour pressure of solution having 40 mole-percent of A in the vapour at equilibrium. ( $P_A^0 = 80 \text{ cm Hg}$ ,  $P_B^0 = 30 \text{ cm Hg}$ )

**Sol.** 
$$\frac{1}{P_{\text{total}}} = \frac{Y_A}{P_A^0} + \frac{Y_B}{P_B^0} = \frac{0.4}{80} + \frac{0.6}{30} = \frac{1}{40}$$

$$P_{\text{total}} = 40 \text{ cm Hg}$$

**Ex.8.** Liquids 'A' and 'B' form an ideal solution. Calculate the molar-fraction of 'A' in vapour form above the liquid solution containing 25 mole-percent of 'A' at equilibrium ( $P_A^0 = 0.2 \text{ atm}$ ,  $P_B^0 = 0.5 \text{ atm}$ )

**Sol.** 
$$Y_A = \frac{P_A}{P_{\text{total}}} = \frac{X_A \cdot P_A^0}{X_A \cdot P_A^0 + X_B \cdot P_B^0} = \frac{0.25 \times 0.2}{0.25 \times 0.2 + 0.75 \times 0.5} = \frac{2}{17}$$

**Ex.9.** Liquids 'A' and 'B' form an ideal solution. At  $80^\circ\text{C}$ ,  $P_A^0 = 0.4 \text{ bar}$  and  $P_B^0 = 0.8 \text{ bar}$ . All the vapour above the liquid solution containing equal moles of both the liquids at equilibrium is collected in another empty vessel and condensed. Now, the condensate is heated to  $80^\circ\text{C}$  and all the vapours above the liquid solution at equilibrium is again collected in another empty vessel and condensed. What is the mole-fraction of 'B' in new condensate?

**Sol.** For the first condensate,

$$\frac{n_B'}{n_A'} = \frac{X_B'}{X_A'} = \frac{Y_B}{Y_A} = \frac{X_B}{X_A} \cdot \frac{P_A^0}{P_B^0} = \frac{n_B}{n_A} \times \frac{P_B^0}{P_A^0}$$

For second condensate,

$$\frac{n_B''}{n_A''} = \frac{X_B''}{X_A''} = \frac{Y_B'}{Y_A'} = \frac{X_B'}{X_A'} \cdot \frac{P_B^0}{P_A^0} = \frac{n_B'}{n_A'} \times \left( \frac{P_B^0}{P_A^0} \right)^2 = \frac{x}{x} \times \left( \frac{0.8}{0.4} \right)^2 = \frac{4}{1}$$

$$\therefore \text{Mole fraction of B} = \frac{4}{5} = 0.8$$

**Note :** For multi-step condensation at constant temperature,

$$\frac{n_B^f}{n_A^f} = \frac{n_B^i}{n_A^i} \cdot \left( \frac{P_B^0}{P_A^0} \right)^n \quad n : \text{number of steps}$$

**Ex.10.** Liquid A & B form an ideal solution. In a cylinder piston arrangement, 2 moles of vapours of liquid A & 3 moles of vapours of liquid B are taken at 0.3 atm.  $P_A^0 = 0.4 \text{ atm}$ ,  $P_B^0 = 0.6 \text{ atm}$ .

- (i) Predict whether vapours will condense or not ?
- (ii) If the vapours are compressed slowly & isothermally, at what pressure  $P^{\text{st}}$  drop of liquid will form
- (iii) If the initial volume of vapours was 10L, at what volume  $P^{\text{st}}$  drop of liquid will form ?
- (iv) What is the composition of  $P^{\text{st}}$  drop of liquid formed ?
- (v) If the vapours are further compressed slowly & isothermally, at what  $P$  almost complete condensation will occur ?
- (vi) What is the composition of last traces of vapours remained ?
- (vii) What is the composition of system at 0.58 atm ?
- (viii) What is the composition of system at 0.51 atm ? Also calculate moles of A & B in liquid & vapour form.
- (ix) At what  $P$ , half of the total amount of vapours will condense ?

**Sol.** (i)  $\frac{1}{P_T} = \frac{Y_A}{P_A^0} + \frac{Y_B}{P_B^0} = \frac{2/5}{0.4} + \frac{3/5}{0.6} \Rightarrow P_{\text{total}} = 0.5 \text{ atm} > 0.3 \text{ atm}$

$\therefore$  100% gas, no condensation

(ii) 0.5 atm.

(iii)  $P_i V_i = P_f V_f$

$$V_f = \frac{0.3 \times 10}{0.5} = 6 \text{ L}$$

(iv)  $P_{\text{total}} = X_A \cdot P_A^0 + X_B \cdot P_B^0$

$$\text{or } 0.5 = X_A \times 0.4 + (1 - X_A) \times 0.6 \Rightarrow X_A = 0.5$$

(v)  $P_T = 0.4 \times 0.4 + 0.6 \times 0.6 = 0.52 \text{ atm}$

**Note:** For a pure liquid, there is a fixed  $P(V.P.)$  below & above which, the system will be 100% gas & 100% liquid, respectively but for a solution, a pressure range exist in which both physical states will be present.

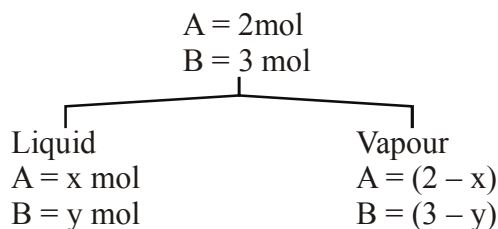
(vi)  $Y_A = \frac{X_A \cdot P_A^0}{P_{\text{total}}} = \frac{0.4 \times 0.4}{0.52} = \frac{4}{13}$

(vii) 100% liquid, A = 2mole and B = 3 mole

(viii)  $P_{\text{total}} = X_A P_A^0 + X_B P_B^0$

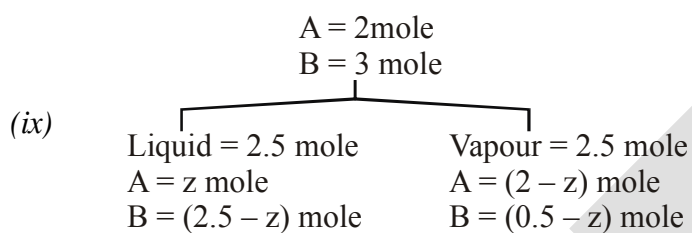
$$0.51 = X_A \times (0.4) + (1 - X_A) \times 0.6 \quad \& \quad Y_A = \frac{X_A P_A^0}{P_{\text{total}}} = \frac{0.45 \times 0.4}{0.51} = 0.35$$

$$X_A = 0.45$$



$$X_A = \frac{9}{20} = \frac{x}{x+y} \quad \text{and} \quad Y_A = \frac{18}{51} = \frac{2-x}{(2-x)+(3-y)}$$

$$\therefore x = 1.09; \quad y = 1.33$$



$$P_T = \frac{z}{2.5} \times 0.4 + \frac{2.5-z}{2.5} \times 0.6$$

$$\frac{2-z}{2.5} = \frac{z \times 0.4}{2.5 \times P_T}$$

$$\text{On solving, } z = 1.12, \quad P_T = 0.5104 \text{ atm}$$

## 6.5 Graphs for ideal Binary solution of liquid A & liquid B :

(Assume  $P_A^0 < P_B^0$ )

### I. Vapour pressure V/s liquid composition

$$P_A = X_A P_A^0 = (1 - X_B) P_A^0$$

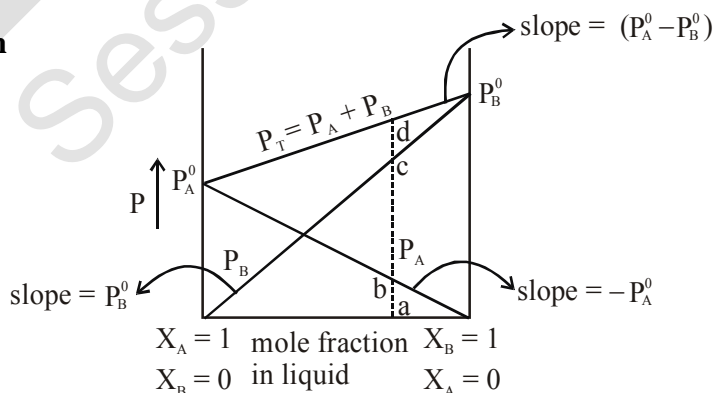
$$P_A = P_A^0 - X_B P_A^0$$

$$P_B = X_B P_B^0$$

$$P_T = X_A P_A^0 + X_B P_B^0 = (1 - X_B) P_A^0 + X_B P_B^0$$

$$\therefore P_T = P_A^0 + X_B (P_B^0 - P_A^0)$$

$$\text{As } P_T = P_A + P_B, \quad \text{ad} = \text{ab} + \text{ac}$$



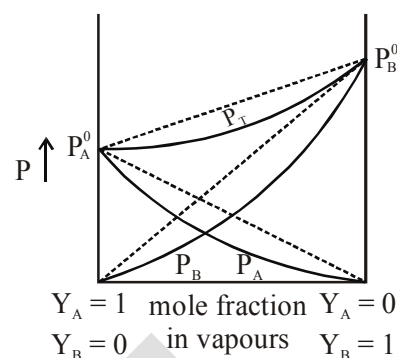
## II. Vapour pressure V/s vapour composition

$$\frac{1}{P_T} = \frac{Y_A}{P_A^0} + \frac{Y_B}{P_B^0}$$

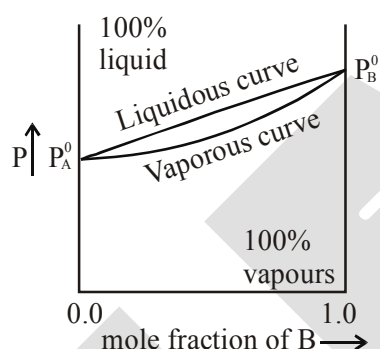
$$\frac{1}{P_T} = \frac{1}{P_A^0} + Y_B \left( \frac{1}{P_B^0} - \frac{1}{P_A^0} \right)$$

$$\frac{1}{y} = c + mx$$

So curve will be rectangular hyperbola.



## III. Vapour pressure V/s composition

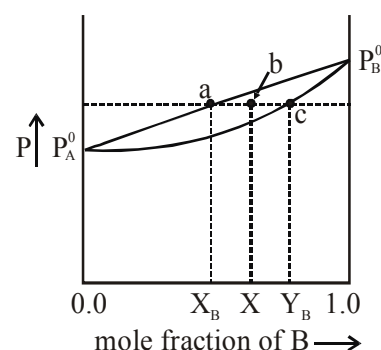


- The V.P. of ideal solution always lie in between the V.P. of pure components.
- Below vaporous curve, the system will be 100% vapour & above liquidous curve, 100% liquid. Both the physical states exist only in between the curves.
- At any composition, the physical state of system may be changed by changing the pressure.
- At any pressure in between  $P_A^0$  and  $P_B^0$ , the physical state of system may be changed by changing the composition.
- Length  $ab \propto$  total moles of vapour

Length  $cb \propto$  total moles of liquid

$$\frac{ab}{cb} = \frac{\text{total moles of vapour}}{\text{total moles of liquid}}$$

$$\text{or } \frac{X - X_B}{Y_B - X} = \frac{n_{A(g)} + n_{B(g)}}{n_{A(l)} + n_{B(l)}} \quad (\text{Lever's rule})$$



### 6.6 Boiling point :

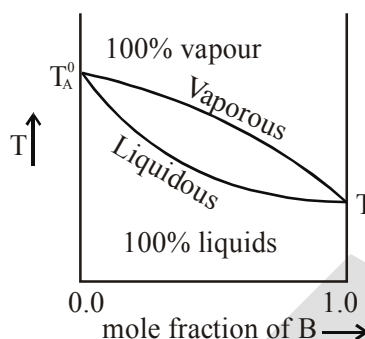
Boiling point of a liquid is the temperature at which the vapour pressure of the liquid becomes equal to the atmospheric pressure.

**Ex.11** Liquid 'A' and 'B' form an ideal solution. At 27°C, the vapour pressure of pure liquids 'A' and 'B' are 0.6 atm and 1.2 atm, respectively. What the coposition of liquid solution boiling at 27°C?

**Sol.**  $P_T = X_A \cdot P_A^0 + X_B \cdot P_B^0$

or  $1 = X_A \times 0.6 + (1 - X_A) \times 1.2 \Rightarrow X_A = \frac{1}{3}$

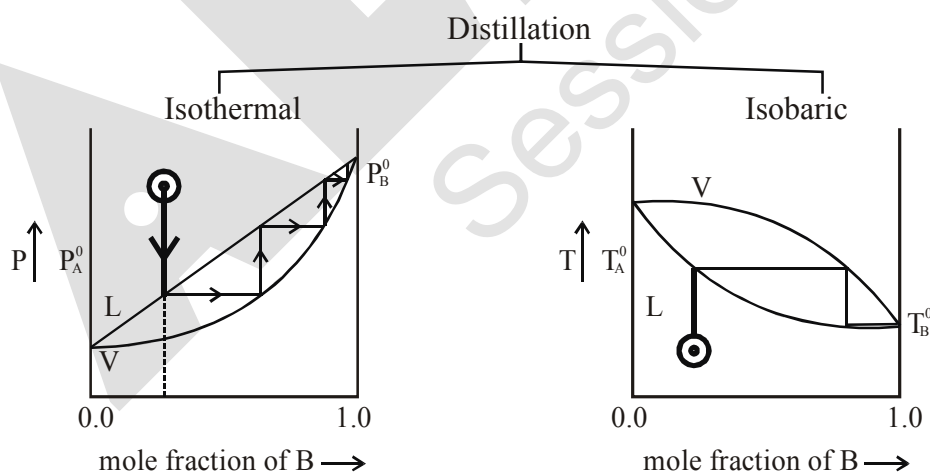
### 6.7 Boiling point curves for ideal binary solution :



- The boiling point of ideal solution always lie in between the boiling points of pure liquids.
- Below liquidus curve, the system is 100% liquid and above vaporous curve, the system is 100% vapour. Both the physical states exist only in between the curves.
- At any composition, the physical state of system may be changed by changing the temperature.
- At any temperature in between  $T_A^0$  and  $T_B^0$ , the physical state of system may be changed by changing the composition.

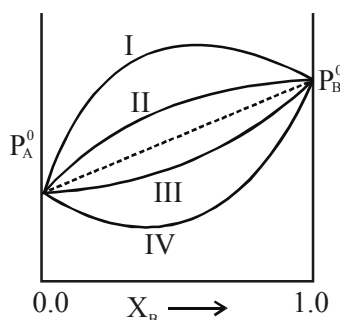
### 6.8 Distillation

It is the method of separation of liquids by converting them into vapours (boiling).



- The separation of liquid by distillation occurs because at any T or P, the composition of distillate or condensate is different than the composition of original liquid.
- With the elimination of vapour above the liquid, the boiling point of residual liquid increases.
- The boiling point of distillate is less than that of original liquid.

## 6.9 Graphs for Non-ideal solutions and azeotropic mixture

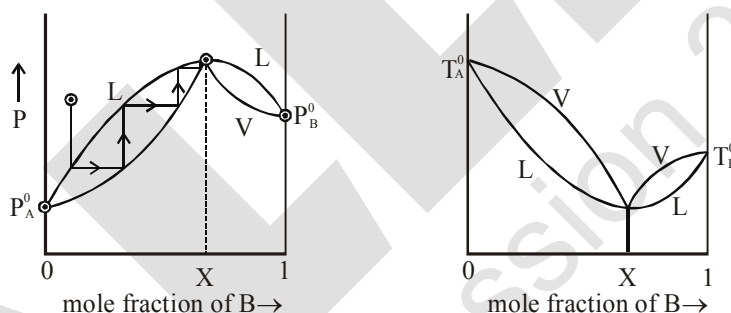


- (I) Large positive deviation :  $(V.P.)_{\text{solution}} > P_B^0$  at some composition
- (II) Small positive deviation :  $P_A^0 < (V.P.)_{\text{solution}} < P_B^0$
- (III) Small negative deviation :  $P_A^0 < (V.P.)_{\text{solution}} < P_B^0$
- (IV) Large negative deviation :  $(V.P.)_{\text{solution}} < P_A^0$  at some composition

## 6.9.1 Konowaloff's rule :

In ideal or non-ideal solution the vapour is always more rich in the component, addition of which in liquid, increase the vapour pressure of solution.

## 6.9.2 Large (+)ve derivation (Minimum boiling azeotrope)



The solution of large positive deviation can not be separated by distillation because at composition 'x', the liquid & vapour composition becomes identical.

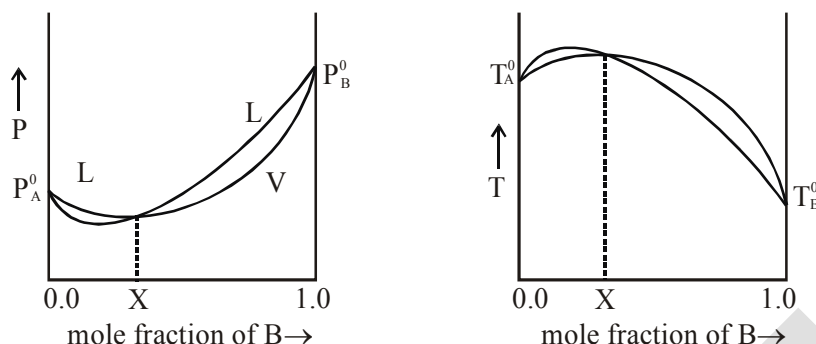
Such solution which can not be separated by distillation are called **azeotropic mixture or constant boiling solution**.

At any composition less than X, traces of pure A may be obtained but not pure B. Similarly at composition greater than X, traces of pure B may be obtained but not pure A.

## Minimum boiling point Azeotropic

| Mixture                | % Composition of azeotrope | Boiling point (pressure = 1atm) |
|------------------------|----------------------------|---------------------------------|
| 1. Water-Ethanol       | 96 Ethanol                 | 78.15°C                         |
| 2. Pyridine-Water      | 57.00 Pyridine             | 92.60°C                         |
| 3. Ethanol-Benzene     | 32.4 Ethanol               | 67.80°C                         |
| 4. Acetic acid-Toluene | 28.0 Acetic acid           | 105.40°C                        |

### 5.9.3 Large (–)ve deviation (Maximum boiling azeotrope)



Maximum boiling point Azeotropic

| Mixture                    | % Composition of azeotrope | Boiling point (pressure = 1 atm) |
|----------------------------|----------------------------|----------------------------------|
| 1. Nitric acid-Water       | 68% Nitric acid            | 125.5°C                          |
| 2. Acetic acid-Pyridine    | 65% Pyridine               | 139.0°C                          |
| 3. Chloroform-Acetone      | 80% Chloroform             | 65.0°C                           |
| 4. Hydrogen chloride-Water | 79.8 Water                 | 108.6°C                          |

**Note :** Azeotrope is not formed in ideal solution or solution of small deviations.

## 7. COLLIGATIVE PROPERTIES

Properties of a solution which depends on the number of solute particles irrespective of their nature, relative to the total number of particles present in solution are called colligative properties.

The following properties are colligative properties of solution :

- Relative lowering of vapour pressure.
- Elevation in boiling point.
- Depression in freezing point.
- Osmotic pressure.

### 7.1 Lowering of vapour pressure :

When a non-volatile solute 'A' is dissolved in a pure solvent 'B', the vapour pressure of the solvent is lowered i.e. the vapour pressure of a solution is always lower than that of pure solvent, because the escaping tendency of solvent molecules decreases.

If at a certain temperature  $P^0$  is the vapour pressure of pure solvent, and  $P_s$  is the vapour pressure of solution then

$$\text{Lowering of vapour pressure} = P^0 - P_s$$

$$\text{Relative lowering of vapour pressure} = \frac{P^0 - P_s}{P^0}$$

from equation (8)

$$\frac{P^0 - P_s}{P^0} = \frac{\Delta P}{P^0} = \frac{n_A}{n_A + n_B} = X_A$$



For a very dilute solution  $n_A \ll n_B$

$$\text{SO} \quad \frac{P^0 - P_s}{P^0} = \frac{n_A}{n_B} = \frac{w_A}{m_A} \times \frac{m_B}{w_B}$$

**Ex.12.** Calculate the vapour pressure lowering caused by addition of 50 g of sucrose (molecular mass = 342) to 500 g of water if the vapour pressure of pure water at 25°C is 23.8 mm Hg.

**Sol.** According to Raoult's law,

$$\frac{p_0 - p_s}{p_0} = \frac{n}{n + N} \quad \text{or} \quad \Delta p = \frac{n}{n + N} \cdot p_0$$

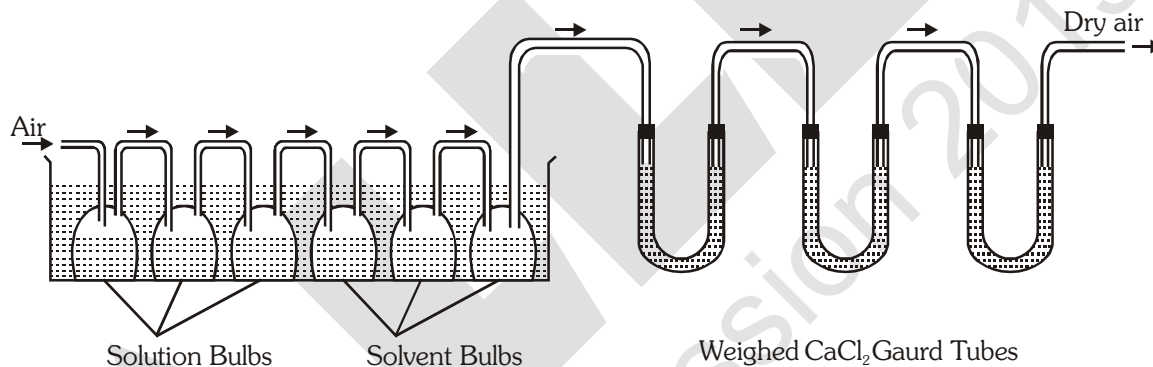
$$\text{Given : } n = \frac{50}{342} = 0.146 ; N = \frac{500}{18} = 27.78 \text{ and } p_0 = 23.8 \text{ mmHg}$$

Substituting the values in the above equation,

$$\Delta p = \frac{0.146}{0.146 + 27.78} \times 23.8 = 0.124 \text{ mm Hg}$$

### 7.1.1 Measurement of Lowering in Vapour Pressure by Dynamic Method (Ostwald and Walker Method)

The apparatus used is shown in Fig. It consists of two sets of bulbs. The first set of three bulbs is filled with solution to half of their capacity and second set of another three bulbs is filled with the pure solvent.



**Fig.** Ostwald and Walker method

Each set is separately weighed accurately. Both sets are connected to each other and then with the accurately weighed set of guard tubes filled with anhydrous calcium chloride or some other dehydrating agents like  $P_2O_5$ , conc.  $H_2SO_4$  etc. The bulbs of solution and pure solvent are kept in a thermostat maintained at a constant temperature.

A current of pure dry air is bubbled through the series of bulbs as shown in fig. The air gets saturated with the vapour in each set of bulbs. The air takes up an amount of vapours proportional to the vapour pressure of the solution first and then it takes up more amount of vapours from the solvent which is proportional to the difference in the vapour pressure of the solvent and the vapour pressure of solution, i.e.,  $p_0 - p_s$ .

The two sets of bulbs are weighed again. The guard tubes are also weighed.

$$\text{Loss in mass in the solution bulbs} \propto p_s$$

Loss in mass in the solvent bulbs  $\propto (p_0 - p_s)$

Total loss in both sets of bulbs  $\propto [p_s + (p_0 - p_s)] \propto p_0$

Total loss in mass of both sets of bulbs is equal to gain in mass of guard tubes.

$$\text{Thus, } \frac{p_0 - p_s}{p_0} = \frac{\text{Loss in mass in solvent bulbs}}{\text{Total loss in mass in both sets of bulbs}} = \frac{\text{Loss in mass in solvent bulbs}}{\text{Gain in mass of guard tubes}}$$

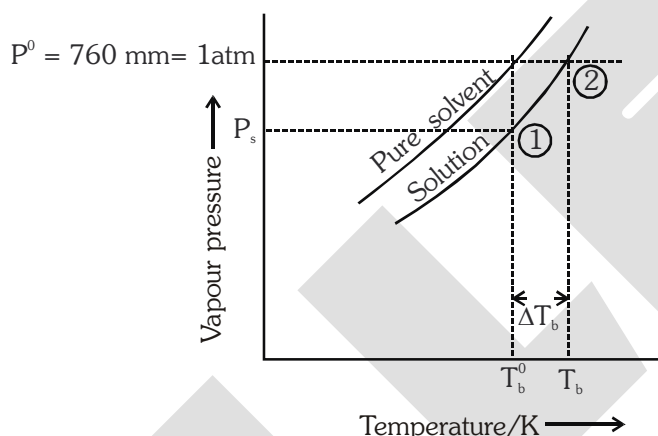
Further, we know from Raoult's law,

$$\frac{p_0 - p_s}{p_0} = \frac{w_A / m_A}{w_A / m_A + w_B / m_B}$$

$$\therefore \frac{\text{Loss in mass of solvent bulbs}}{\text{Gain in mass of guard tubes}} = \frac{w_A / m_A}{w_A / m_A + w_B / m_B}$$

## 6.2 Elevation in boiling point (Ebullioscopy) :

solvent (l)  $\rightleftharpoons$  solvent (g)



The vapour pressure curve for solution lies below the curve for pure solvent.

$\Delta T_b$  denotes the elevation of boiling point of a solution.

When a non-volatile solute A is dissolved in a pure solvent B, its vapour pressure decreases and hence the boiling point increases. The difference  $\Delta T_b$  of boiling points of the solution and pure solvent is called elevation in boiling point.

If  $T_b^0$  is the boiling point of pure solvent and  $T_b$  is the boiling point of the solution then,  $T_b > T_b^0$

and the elevation in boiling point  $\Delta T_b = T_b - T_b^0$

Experiments have shown that for dilute solutions, the elevation of boiling point ( $\Delta T_b$ ) is directly proportional to the molal concentration of the solute in a solution. Thus

$$\Delta T_b \propto m$$

$$\text{or } \Delta T_b = K_b \cdot m$$

where  $K_b$  = boiling point elevation constant or molal elevation constant or ebullioscopic constant.

Molal elevation constant is characteristic of a particular solvent and can be calculated from the thermodynamical relationship.

$$K_b = \frac{RT_b^2 \cdot M}{1000 \Delta H_{\text{vap}}}$$

where, R is molar gas constant = 2 cal/mol-K, M = molar mass of solvent

$T_b$  is the boiling point of the pure solvent (in K)

and  $\Delta H_{\text{vap}}$  is the latent heat of vaporisation of pure solvent

For water 
$$K_b = \frac{2 \times (373)^2}{1000 \times 540} = 0.515 \text{ K}\cdot\text{kg/mol}$$

The molal elevation constant for some common solvents are given in the following table

| Solvent              | B.P. (°C) | Molal elevation constant |
|----------------------|-----------|--------------------------|
| Water                | 100.0     | 0.52                     |
| Acetone              | 56.0      | 1.70                     |
| Chloroform           | 61.2      | 3.63                     |
| Carbon tetrachloride | 76.8      | 5.03                     |
| Benzene              | 80.0      | 2.53                     |
| Ethyl alcohol        | 78.4      | 1.20                     |

**Ex.13.** 0.15 g of a substance dissolved in 15 g of solvent boiled at a temperature higher by 0.216°C than that of the pure solvent. What is the molecular weight of the substance. [ $K_b$  for solvent = 2.16 K·kg/mol]

**Sol.** Given :  $K_b = 2.16^\circ\text{C}$ ,  $w = 0.15 \text{ g}$ ,  $\Delta T_b = 0.216^\circ\text{C}$ ,  $W = 15 \text{ g}$

$$\Delta T_b = \text{molality} \times K_b$$

$$\Delta T_b = \frac{w}{m \times W} \times 1000 \times K_b$$

$$0.216 = \frac{0.15}{m \times 15} \times 1000 \times 2.16$$

$$m = \frac{0.15 \times 1000 \times 2.16}{0.216 \times 15} = 100$$

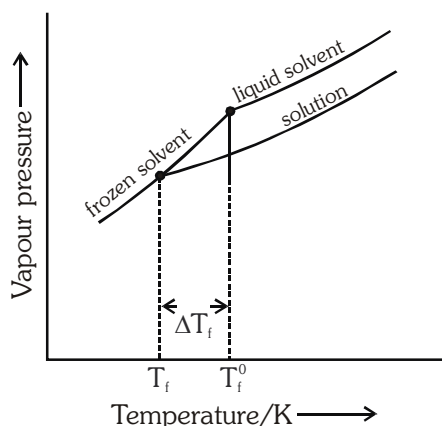
**Ex.14** The rise in boiling point of a solution containing 1.8 g glucose in 100 g of a solvent is 0.1°C. The molal elevation constant of the liquid is –

**Sol.**  $\Delta T_b = 0.1^\circ\text{C}$ ,  $m = 180$ ,  $W = 100$ ,  $w = 1.8$

$$K_b = \frac{\Delta T_b \times m \times W}{1000 \times w} = \frac{180 \times 0.1 \times 100}{1000 \times 1.8} = 1.0$$

### 7.3 Depression in freezing point (Cryoscopy) :

The freezing point of a liquid is that temperature at which the liquid and its solid state exist in equilibrium with each other. It may also be defined as the temperature at which the liquid and solid states of a substance have the same vapour pressure.



When a non-volatile non-electrolyte is dissolved in a pure solvent, the vapour pressure of the solvent is lowered and it become equal to that of solid solvent at lower temperature.

If  $T_f^0$  is the freezing point of pure solvent and ( $T_f$ ) is the freezing point of its solution then,

$$T_f < T_f^0$$

The difference in the freezing point of pure solvent and solution is the depression of freezing point ( $\Delta T_f$ ). Thus,

$$T_f^0 - T_f = \Delta T_f$$

Similar to elevation in boiling point, depression in freezing point for dilute solution is directly proportional to its molality,

$$\Delta T_f \propto m$$

or 
$$\Delta T_f = K_f m$$

where  $K_f$  is called freezing point depression constant or molal depression constant or cryoscopic constant.

$K_f$  is characteristic of a particular solvent and can be calculated from the thermodynamical relationship

$$K_f = \frac{R \cdot T_f^{02} \cdot M}{1000 \cdot \Delta H_{\text{fus}}}$$

where,  $T_f^0$  is the freezing point of pure solvent in (Kelvin) and  $\Delta H_{\text{fus}}$  is the latent heat of fusion pure solvent.

For water,

$$K_f = \frac{0.002 \times (273)^2}{80} = 1.86 \text{ K}\cdot\text{kg/mol}$$

The molal depression constant for some common solvents are given in the following table

| Solvent              | F.P.(°C) | Molal depression solvents |
|----------------------|----------|---------------------------|
| Water                | 0.0      | 1.86                      |
| Ethyl alcohol        | - 114.6  | 1.99                      |
| Chloroform           | - 63.5   | 4.79                      |
| Carbon tetrachloride | - 22.8   | 31.8                      |
| Benzene              | 5.5      | 5.12                      |
| Camphor              | 179.0    | 39.70                     |

**Ex.15.** If freezing point of a solution prepared from 1.25 g of a non electrolyte and 20 g of water is 271.9 K, the molar mas of the solute will be – ( $K_f$  of water = 1.86 K-kg/mol)

**Solution :** Given  $T_f = 271.9$  K

$$w = 1.25 \text{ g} \quad W = 20 \text{ g} \quad K_f = 1.86$$

$$\Delta T_f = T_f^0 - T_f = 273 - 271.9 = 1.1 \text{ K}$$

$$\Delta T_f = \text{molality} \times K_f$$

$$\Rightarrow \Delta T_f = \frac{w}{m \times W} \times 1000 \times K_f$$

$$\text{or } m = \frac{w \times 1000 \times K_f}{\Delta T_f \times W} = \frac{1.25 \times 1000 \times 1.86}{1.1 \times 20} = 105.68 \text{ mol/kg}$$

**Ex.16.** Molal depression constant for water is 1.86. What is freezing point of a 0.05 molal solution of a non electrolyte in water ? ( $K_f$  of water = 1.86 K-kg/mol)

**Solution :**  $\Delta T_f = \text{molality} \times K_f$

$$= 0.05 \times 1.86 = 0.093^\circ\text{C}$$

$$T_f = T_f^0 - 0.093 = 0 - 0.093$$

$$T_f = -0.093^\circ\text{C}$$

**Ex.17.** 2m aqueous urea solution is cooled to  $-7.44^\circ\text{C}$ . Calculate the mass percent of water present in solution, which will separate as ice, ( $K_f$  of water = 1.86 K-kg/mol)

**Sol.** Let the initial mass of water in the solution = 1kg

$$\therefore \text{Moles of solute} = 2$$

$$\text{Now, } \Delta T_f = K_f \cdot m = K_f \cdot \frac{n_{\text{solute}}}{K_{\text{g solvent}}} \text{ or } 7.44 = 1.86 \times \frac{2}{K_{\text{g solvent}}}$$

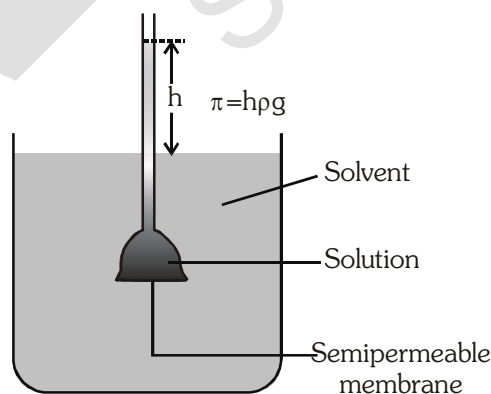
$$\therefore K_{\text{g solvent}} \text{ left in the solution} = 0.5$$

$$\therefore \text{Mass percent of water separated as ice} = \frac{0.5}{1} \times 100 = 50\%$$

## 7.4 Osmosis and osmotic pressure :

### 7.4.1 Osmosis :

Osmosis is defined as the spontaneous flow of solvent molecules through semipermeable membrane from a pure solvent to solution.



Level of solution rises in the funnel due to osmosis of solvent

### 7.4.2 Semi-permeable membrane (SPM) :

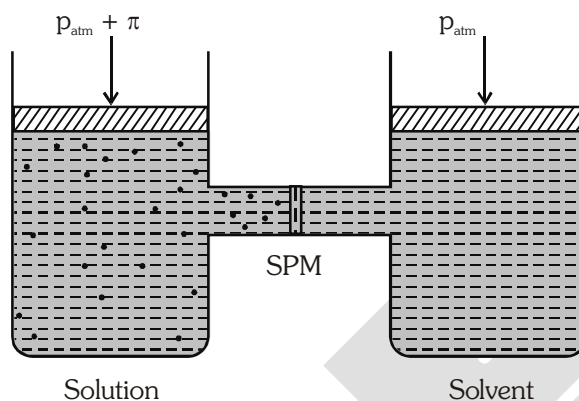
There are the membranes (substances) which allow selective movement of particles across them. For a solution of solid solute in a liquid solvent, ideal SPM allow free movement of solvent particles across it, but not solute particles. These membranes contain a network of submicroscopic holes or pores through which small solvent molecules may pass but not the bigger solute particle.

### 7.4.3 Osmotic pressure ( $\pi$ ) :

It is the pressure which should be applied on the solution to just prevent osmosis or The hydrostatic pressure built up on the solution which just stops the osmosis.

osmotic pressure = hydrostatic pressure

$$\pi = \rho gh$$



The excess pressure equal to the osmotic pressure must be applied on the solution side to prevent osmosis

### 7.4.4 Van't Hoff laws :

- (i) The osmotic pressure ( $\pi$ ) of a solution is directly proportional to its molar concentration ( $C$ ), when the temperature is kept constant. (Van't Hoff-Boyle's law)  
thus  $\pi \propto C$  (when temperature is constant)
- (ii) Concentration remaining same, the osmotic pressure of a dilute solution is directly proportional to its absolute temperature ( $T$ ). (Van't Hoff-Charles's law)

$$\pi \propto T \quad (\text{when } C \text{ is constant})$$

Combining the two laws, i.e., when concentration and temperature both are changing, the osmotic pressure will be given by :

$$\pi \propto C.T \quad \text{or} \quad \pi = CRT$$

Where  $R$  = Universal gas constant.

### 7.4.5 Isotonic or iso-osmotic solution :

Solutions which have the same osmotic pressures at a given temperature are called isotonic or iso-osmotic solutions

When isotonic solutions are separated by semipermeable membrane, no osmosis occurs between them. For example, the osmotic pressure associated with the fluid inside the blood cell is equivalent to that of 0.9% (mass/volume) sodium chloride solution, called normal saline solution and it is safe to inject intravenously.

On the other hand, if we place the cells in a solution containing more than 0.9% (mass/volume) sodium chloride, water will flow out of the cells and they would shrink. Such a solution is called **hypertonic**. If the salt concentration is less than 0.9% (mass/volume), the solution is said to be **hypotonic**. In this case, water will flow into the cells if placed in this solution and they would swell.

**Ex.18.** A cane sugar solution has an osmotic pressure of 2.46 atm at 300 K. What is the strength of the solution.

**Sol.**  $\pi = CRT$

$$\text{or } C = \frac{\pi}{RT} = \frac{2.46}{300 \times 0.0821} = 0.1 \text{ M}$$

**Ex.19** A solution containing 8.6 g urea in one litre was found to be isotonic with 0.5% (wt./vol.) solution of an organic, non-volatile solution. The molecular weight of latter is

**Sol.** Solutions are isotonic

$$\text{so } \pi_1 = \pi_2$$

$$\frac{n_1}{V_1} RT = \frac{n_2}{V_2} RT \quad \{R \text{ \& } T \text{ are constant}\}$$

$$\text{so, } \frac{n_1}{V_1} = \frac{n_2}{V_2}$$

$$\text{or } \left( \frac{w_1}{m_1 \times v_1} \right)_{\text{urea}} = \left( \frac{w_2}{m_2 \times v_2} \right)_{\text{organic}}$$

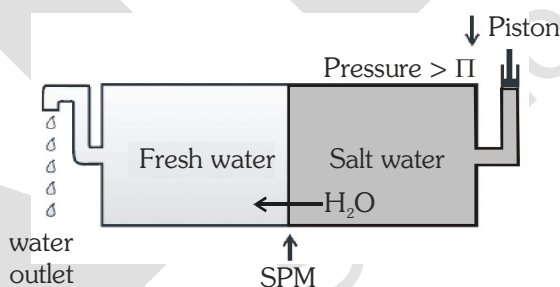
$$\text{or } \frac{8.6}{60 \times 1000} = \frac{0.5}{m_2 \times 100}$$

$$m_2 = 34.89 \text{ gm/mol}$$

## 7.5 Reverse Osmosis and water purification :

If external pressure greater than osmotic pressure is applied, the flow of solvent molecules can be made to proceed from solution towards pure solvent, i.e., in reverse direction of the ordinary osmosis.

Reverse osmosis is used for the desalination of sea water for getting fresh drinking water.



Reverse osmosis occurs when a pressure larger than the osmotic pressure is applied to the solution.

## 8 Abnormal colligative properties :

It has been observed that difference in the observed and calculated molecular masses of solute is due to association or dissociation of solute molecules in solution. It results in a change in the number of particles in solution.

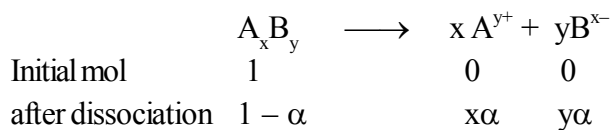
Van't Hoff in 1880, introduced a factor, called Van't Hoff factor (*i*). The factor '*i*' is defined as

$$i = \frac{\text{observed colligative property}}{\text{Calculated colligative property}} = \frac{\text{Normal molecular mass}}{\text{observed molecular mass.}}$$

$$= \frac{\text{total number of particles after dissociation / association}}{\text{Number of particles initially taken}}$$

In case of association of solute particles in solution, the observed molecular weight of solute being more than the normal, the value of factor 'i' is less than unity (i.e.  $i < 1$ ), while for dissociation the value of i is greater than unity (i.e.  $i > 1$ ), because the observed molecular weight has lesser value than normal molecular weight.

### 8.1 Calculation of 'i' in case of dissociation

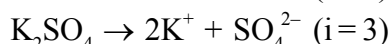
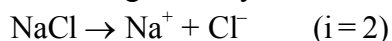


$$\text{Total no. of solute particles} = 1 - \alpha + x\alpha + y\alpha = 1 - \alpha + \alpha(x + y)$$

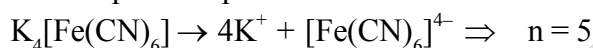
$$\text{or } i = 1 - \alpha + n\alpha \quad [\text{where } x + y = n (\text{total ions.})]$$

$$\text{or } i = 1 + \alpha(n - 1)$$

For strong electrolytes:  $\alpha = 1$  or 100%, so  $i = n$  (total no. of ions)



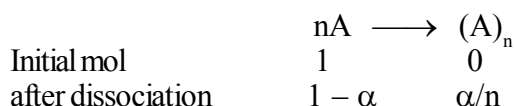
For complex compound



| S. No. | Solute type                                                         | Example                                                                                    | Ionisation                                                                                                                                                                                                                | No. of particles in the solution from 1 mole solute (n) | van't Hoff factor ('i')        | Abnormal molecular mass                                                            |
|--------|---------------------------------------------------------------------|--------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------|--------------------------------|------------------------------------------------------------------------------------|
| 1.     | Non-electrolyte                                                     | Urea, sucrose, glucose, fructose                                                           | —                                                                                                                                                                                                                         | 1                                                       | 1                              | $m_{\text{normal}}$                                                                |
| 2.     | Binary electrolyte AB type                                          | NaCl, KCl, HCl<br>$\text{CH}_3\text{COOH}$<br>$\text{NH}_4\text{OH}$ , NaOH<br>etc.        | $\text{AB} \rightleftharpoons \text{A}^+ + \text{B}^-$<br>$1 - \alpha \quad \alpha \quad \alpha$                                                                                                                          | 2                                                       | $1 + \alpha$                   | $\frac{m_{\text{normal}}}{1 + \alpha}$                                             |
| 3.     | Ternary electrolyte $\text{AB}_2$ type or $\text{A}_2\text{B}$ type | $\text{CaCl}_2$ , $\text{BaCl}_2$<br>$\text{H}_2\text{SO}_4$ , $\text{K}_2[\text{PtCl}_6]$ | $\text{AB}_2 \rightleftharpoons \text{A}^{2+} + 2\text{B}^-$<br>$1 - \alpha \quad \alpha \quad 2\alpha$<br>$\text{A}_2\text{B} \rightleftharpoons 2\text{A}^+ + \text{B}^-$<br>$1 - \alpha \quad 2\alpha \quad \alpha$    | 3<br>3                                                  | $1 + 2\alpha$<br>$1 + 2\alpha$ | $\frac{m_{\text{normal}}}{1 + 2\alpha}$<br>$\frac{m_{\text{normal}}}{1 + 2\alpha}$ |
| 4.     | Quaternary electrolyte $\text{AB}_3$ or $\text{A}_3\text{B}$ type   | $\text{AlCl}_3$ , $\text{K}_3[\text{Fe}(\text{CN})_6]$                                     | $\text{AB}_3 \rightleftharpoons \text{A}^{3+} + 3\text{B}^-$<br>$1 - \alpha \quad \alpha \quad 3\alpha$<br>$\text{A}_3\text{B} \rightleftharpoons 3\text{A}^+ + \text{B}^{3-}$<br>$1 - \alpha \quad 3\alpha \quad \alpha$ | 4<br>4                                                  | $1 + 3\alpha$<br>$1 + 3\alpha$ | $\frac{m_{\text{normal}}}{1 + 3\alpha}$<br>$\frac{m_{\text{normal}}}{1 + 3\alpha}$ |
| 5.     | General electrolyte $\text{AB}_{n-1}$                               | One mole of solute giving 'n' ions in the solution                                         | $\text{AB}_{n-1} \rightleftharpoons \text{A}^{+(n-1)} + (n-1)\text{B}^-$<br>$1 - \alpha \quad \alpha \quad (n-1)\alpha$                                                                                                   | n                                                       | $1 + (n-1)\alpha$              | $\frac{m_{\text{normal}}}{[1 + (n-1)\alpha]}$                                      |



## 8.2 Calculation of 'i' in case of association



$$i = \frac{1 - \alpha + \frac{\alpha}{n}}{n}, \quad \alpha = \text{degree of association}$$

$$i = 1 + \alpha \left( \frac{1}{n} - 1 \right)$$

**Ex.20.** Determine the amount of  $\text{CaCl}_2$  ( $i = 2.47$ ) dissolved in 2.5 litre of water such that its osmotic pressure is 0.75 atm at  $27^\circ\text{C}$ .

**Sol.** We know that,

$$\pi = i \frac{n}{V} RT \Rightarrow \pi = i \frac{w}{MV} RT$$

$$\Rightarrow w = \frac{\pi MV}{iRT} = \frac{0.75 \times 111 \times 2.5}{2.47 \times 0.0821 \times 300} = 3.42 \text{ g}$$

Hence, the required amount of  $\text{CaCl}_2$  is 3.42 g.

**Ex.21** 19.5 g of  $\text{CH}_2\text{FCOOH}$  is dissolved in 500 g of water. The depression in the freezing point of water observed is  $1.0^\circ\text{C}$ . Calculate the van't Hoff factor and dissociation constant of fluoroacetic acid.

**Sol.** It is given that :

$$w_1 = 500 \text{ g}$$

$$w_2 = 19.5 \text{ g}$$

$$K_f = 1.86 \text{ K kg mol}^{-1}$$

$$\Delta T_f = 1 \text{ K}$$

We know that :

$$M_2 = \frac{K_f \times w_2 \times 1000}{\Delta T_f \times w_1} = \frac{1.86 \text{ K kg mol}^{-1} \times 19.5 \text{ g} \times 1000 \text{ g kg}^{-1}}{500 \text{ g} \times 1 \text{ K}} = 72.54 \text{ mol}^{-1}$$

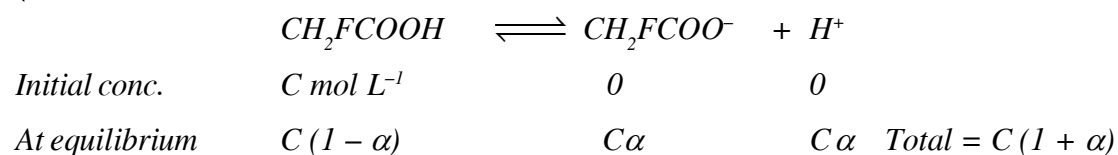
Therefore, observed molar mass of  $\text{CH}_2\text{FCOOH}$ ,  $(M_2)_{\text{obs}} = 72.54 \text{ mol}$

The calculated molar mass of  $\text{CH}_2\text{FCOOH}$  is :

$$(M_2)_{\text{cal}} = 14 + 19 + 12 + 16 + 16 + 1 = 78 \text{ g mol}^{-1}$$

$$\text{Therefore, van't Hoff factor, } i = \frac{(M_2)_{\text{cal}}}{(M_2)_{\text{obs}}} = \frac{78 \text{ g mol}^{-1}}{72.54 \text{ g mol}^{-1}} = 1.0753$$

Let  $\alpha$  be the degree of dissociation of  $\text{CH}_2\text{FCOOH}$



$$\therefore i = \frac{C(1 + \alpha)}{C}$$

$$\Rightarrow i = 1 + \alpha \Rightarrow \alpha = i - 1$$

$$= 1.0753 - 1 = 0.0753$$

Now, the value of  $K_a$  is given as :

$$K_a = \frac{[\text{CH}_2\text{FCOO}^-][\text{H}^+]}{[\text{CH}_2\text{FCOOH}]} = \frac{C\alpha \cdot C\alpha}{C(1 - \alpha)} = \frac{C\alpha^2}{1 - \alpha}$$

Taking the volume of the solution as 500 mL. We have the concentration : 19.5 M

$$C = \frac{78}{500} \times 1000 \text{ M} = 0.5 \text{ M}$$

$$\text{Therefore, } K_a = \frac{C\alpha^2}{1 - \alpha}$$

$$= \frac{0.5 \times (0.0753)^2}{1 - 0.0753} = \frac{0.5 \times 0.00567}{0.9247} = 0.00307 \text{ (approximately)} = 3.07 \times 10^{-3}$$

## EXERCISE # S-I

*(Raoult's law)*

- At 25°C, the vapour pressure of methyl alcohol is 96.0 torr. What is the mole fraction of  $\text{CH}_3\text{OH}$  in a solution in which the (partial) vapor pressure of  $\text{CH}_3\text{OH}$  is 24.0 torr at 25°C?
- The vapour pressure of ethanol and methanol are 44.0 mm and 88.0 mm Hg respectively. An ideal solution is prepared at the same temperature by mixing 69 g of ethanol with 40 g of methanol. Calculate total vapour pressure of the solution.
- Liquids 'A' and 'B' form an ideal solution. The vapour pressure of solution containing equal moles of both liquids is 80 cm Hg. At the same temperature, the vapour pressure of solution containing 25 mole percent of liquid 'A' is 70 cm Hg. Calculate  $P_A^0$  and  $P_B^0$ .
- Liquids 'A' and 'B' form an ideal solution. Calculate the mole-fraction of 'A' in the vapours above the liquid solution containing the liquids 'A' and 'B' in 2 : 3 mole ratio, at equilibrium.  
[Given :  $P_A^0 = 0.4$  atm,  $P_B^0 = 0.8$  atm]
- Liquids 'P' and 'Q' form an ideal solution. At equilibrium, the vapours contain 40% molecules of 'P'. Calculate the vapour pressure of solution.  
[Given :  $P_P^0 = 0.4$  bar,  $P_Q^0 = 0.6$  bar]
- Liquids 'X' and 'Y' form an ideal solution. The vapour pressure of solution may be expressed as :  $P[\text{cmHg}] = (80 - 25x)$ , where 'x' is the mole-fraction of liquid 'X' in the liquid solution at equilibrium. Calculate the vapour pressures of pure liquids 'X' and 'Y'.
- Liquid 'R' and 'S' form an ideal solution. The mole-fraction of 'R' in liquid and vapour phases at equilibrium are 0.25 and 0.40, respectively. If the vapour pressure of solution is 0.50 bar, calculate  $P_R^0$  and  $P_S^0$ .

*Colligative properties*

- The vapour pressure of pure liquid solvent A is 0.80 atm. When a nonvolatile substance B is added to the solvent its vapour pressure drops to 0.60 atm. What is the mole fraction of component B in the solution?
- Calculate the relative lowering in vapour pressure if 100 g of a nonvolatile solute (mol.wt. 100) are dissolved in 432 g water.
- The vapour pressure of pure benzene at 30°C is 640 mm of Hg and the vapour pressure of a solution of a solute in  $\text{C}_6\text{H}_6$  at the same temperature is 624 mm of Hg. Calculate molality of solution.
- The vapour pressure of pure benzene at a certain temperature is 640 mm of Hg. A nonvolatile nonelectrolyte solid weighing 2.175 g is added to 39.0 of benzene. The vapour pressure of the solution is 600 mm of Hg. What is molecular weight of solid substance?
- The vapour pressure of water is 17.54 mm Hg at 293 K. Calculate vapour pressure of 0.5 molal solution of a solute in it.
- When 10.5 g of a nonvolatile substance is dissolved in 742 g of ether, its boiling point is raised 0.25°C. What is the molecular weight of the substance? Molal boiling point constant for ether is 2.12°C·kg/mol.
- Calculate the molal elevation constant,  $K_b$  for water and the boiling point of 0.1 molal urea solution. Latent heat of vaporisation of water is 9.72 kcal mol<sup>-1</sup> at 373.15 K.  $[(373.15)^2 = 258 \times 540]$

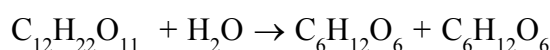
15. Pure benzene freeze at  $5.45^{\circ}\text{C}$ . A solution containing 6.72 g of  $\text{C}_2\text{H}_2\text{Cl}_4$  in 120 g of benzene was observed to freeze at  $3.75^{\circ}\text{C}$ . What is the molal freezing point constant of benzene?
16. The freezing point of a solution containing 2.40 g of a compound in 60.0 g of benzene is  $0.10^{\circ}\text{C}$  lower than that of pure benzene. What is the molecular weight of the compound? ( $K_f$  is  $5.12^{\circ}\text{C/m}$  for benzene)
17. Normal boiling point of diethyl ether is  $327^{\circ}$  and at 190 mmHg boiling points in  $27^{\circ}\text{C}$ . What is the value of  $\Delta H_{\text{vap}}^{\circ}$  in kJ/mole.  
(Use :  $R = 8.3 \text{ J/K-mole}$ ,  $\ln 2 = 0.7$ )
18. A 6.84% solution (w/v) of cane-sugar (Mol. weight = 342) is isotonic with 0.8%(w/v) solution of non-volatile solute. Find molecular weight of solute.
19. Calculate the osmotic pressure of 12% (w/v) aq. urea solution at  $27^{\circ}\text{C}$ .
20. Calculate the osmotic pressure of a solution containing 18 gm glucose and 17.1 gm canesugar ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) per litre, at  $27^{\circ}\text{C}$ .
21. A storage battery contains a solution of  $\text{H}_2\text{SO}_4$  38% by weight. What will be the Van't Hoff factor if the  $\Delta T_{\text{f(experiment)}}$  is 22.8K. [Given  $K_f = 1.86 \text{ mol}^{-1} \text{ Kg}$ ]
22. A certain mass of a substance, when dissolved in 100 g  $\text{C}_6\text{H}_6$ , lowers the freezing point by  $1.28^{\circ}\text{C}$ . The same mass of solute dissolved in 100g water lowers the freezing point by  $1.40^{\circ}\text{C}$ . If the substance has normal molecular weight in benzene and is completely ionized in water, into how many ions does it dissociate in water?  $K_f$  for  $\text{H}_2\text{O}$  and  $\text{C}_6\text{H}_6$  are 1.86 and  $5.12 \text{ K kg mol}^{-1}$ .
23. 2.0 g of benzoic acid dissolved in 25.0g of benzene shows a depression in freezing point equal to 1.96K. Molal depression constant ( $K_f$ ) of benzene is  $4.9 \text{ K.kg.mol}^{-1}$ . What is the percentage association of the acid?
24. A decimolar solution of potassium ferrocyanide is 50% (w/v) dissociated at 300K. Calculate the osmotic pressure of the solution. ( $R=8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ )
25. A 1.2% solution (w/v) of NaCl is isotonic with 7.2% solution (w/v) of glucose. Calculate degree of ionization and Van't Hoff factor of NaCl.

#### Henry's law

26. How many gm  $\text{O}_2$  gas will dissolve in 100 gm water at 9 bar and  $27^{\circ}\text{C}$ ? ( $K_H = 40 \text{ Kbar}$ )
27. The Henry law constant for dissolution of a gas in aqueous medium is  $3 \times 10^2 \text{ atm}$ . At what partial pressure of the gas (in atm), the molality of gas in aqueous solution will be  $\frac{5}{9} \text{ m}$ .

## EXERCISE # S-II

- At 90°C, the vapour pressure of toluene is 400 torr and that of  $\sigma$ -xylene is 150 torr. What is the composition of the liquid mixture that boils at 90°C, when the pressure is 0.50 atm? What is the composition of vapour produced?
- The vapour pressure of an aqueous solution of glucose is 750 mm Hg at 373 K. Calculate molality and mole fraction of solute.
- Calculate the amount of ice that will separate out of cooling a solution containing 50g of ethylene glycol in 200 g water to -9.3°C. ( $K_f$  for water = 1.86 K mol<sup>-1</sup> kg)
- A solution of crab hemocyanin, a pigmented protein extracted from crabs, was prepared by dissolving 0.750 g in 125 cm<sup>3</sup> of an aqueous medium. At 4°C an osmotic pressure rise of 2.77 mm of the solution was observed. The solution had a density of 1.013 g/cm<sup>3</sup>. Determine the molecular weight of the protein. ( $g = 10 \text{ m/s}^2$ )
- The vapour pressure of an aqueous solution is found to be 750 torr at certain temperature 'T'. If 'T' is the temperature at which pure water boils under atmospheric pressure, calculate the atmospheric pressure. The boiling point of solution is 101.04°C. ( $K_b = 0.52 \text{ K kg mol}^{-1}$ ).
- How many grams of sucrose (mol. wt. = 342) should be dissolved in 100 gm water in order to produce a solution with 105°C difference between the freezing point & boiling point temperature at 1 atm? (Unit:  $K_f = 2 \text{ K kg mol}^{-1}$ ;  $k_b = 0.5 \text{ K kg mol}^{-1}$ )
- An aqueous solution containing 288 gm of a non-volatile compound having the stoichiometric composition  $C_xH_{2x}O_x$  in 90 gm water boils at 101.36°C at 1.00 atmospheric pressure. What is the molecular formula?  $K_b(H_2O) = 0.52 \text{ K mol}^{-1} \text{ kg}$
- A complex is represented as  $CoCl_3 \cdot xNH_3$ . It's 0.1 molal solution in a solution shows  $\Delta T_f = 0.558^\circ\text{C}$ .  $K_f$  for  $H_2O$  is 1.86 K mol<sup>-1</sup> kg. Assuming 100% ionisation of complex and coordination no. of Co is six, calculate formula of complex.
- Phenol associates in benzene to a certain extent to form a dimer. A solution containing  $18.8 \times 10^{-3} \text{ kg}$  phenol in 1 kg of benzene has its freezing point depressed by 0.768 K. Calculate the fraction of phenol that has dimerised.  $K_f$  for benzene = 5.12 kg mol<sup>-1</sup> K.
- The molar volume of liquid benzene (density = 0.877 g ml<sup>-1</sup>) increases by a factor of 2750 as it vaporizes at 20°C and that of liquid toluene (density = 0.867 g ml<sup>-1</sup>) increases by a factor of 7720 at 20°C. A Solution of benzene & toluene has a vapour pressure of 46.0 torr. Find the mole fraction of benzene in the vapour above the solution.
- A solution of 0.1 M  $CH_3COOH$  is placed between parallel electrodes of cross-section area 4cm<sup>2</sup>, separated by 2cm. For this solution resistance measured is 100Ω. If the elevation in boiling point of the 0.1 M  $CH_3COOH$  solution is 'x'K, then the value of (160x) is.  
 $K_b = 0.5 \text{ K kg/mol}$ ;  $\wedge_m^\infty(H^+) = 300 \text{ Scm}^2 \text{ mole}^{-1}$ ;  $\wedge_m^\infty(CH_3COO^-) = 100 \text{ Scm}^2 \text{ mole}^{-1}$
- Cane sugar undergoes the inversion as follow



If solution of 0.025 moles of sugar in 200 gm of water show depression in freezing point 0.372°C, then what % sucrose has inverted. ( $K_f(H_2O) = 1.86 \text{ K kg mol}^{-1}$ )

13. When 0.1 M  $\text{Pb}(\text{NO}_3)_2$  solution is titrated with 0.1 M KI solution then what will be the osmotic pressure (in atm) of solution when equivalence point is reached at 300 K .

(Take :  $R = 0.08 \text{ atm L/mol-k}$ )

14. Using the following information determine the boiling point of a mixture contains 1560 gm benzene and 1125 gm chlorobenzene, when the external pressure is 1000 torr. Assume the solution is ideal.

| Temperature ( $^{\circ}\text{C}$ ) | Vapour pressure<br>of benzene(torr) | Vapour pressure of<br>chlorobenzene(torr) |
|------------------------------------|-------------------------------------|-------------------------------------------|
| 80                                 | 750                                 | 120                                       |
| 90                                 | 1000                                | 200                                       |
| 100                                | 1350                                | 300                                       |
| 110                                | 1800                                | 400                                       |
| 120                                | 2200                                | 540                                       |

15. The cryoscopic constant for acetic acid is 3.6 K kg/mol. A solution of 1 g of a hydrocarbon in 100 g of acetic acid freezes at  $16.14^{\circ}\text{C}$  instead of the usual  $16.60^{\circ}\text{C}$ . The hydrocarbon contains 92.3% carbon. What is the molecular formula?

## EXERCISE # O-I

Single correct :

- The boiling point of  $C_6H_6$ ,  $CH_3OH$ ,  $C_6H_5NH_2$  and  $C_6H_5NO_2$  are  $80^\circ C$ ,  $65^\circ C$ ,  $184^\circ C$  and  $212^\circ C$  respectively which will show highest vapour pressure at room temperature :  
(A)  $C_6H_6$  (B)  $CH_3OH$  (C)  $C_6H_5NH_2$  (D)  $C_6H_5NO_2$
- Mole fraction of A vapours above the solution in mixture of A and B ( $X_A = 0.4$ ) will be  
[Given :  $P_A^\circ = 100 \text{ mm Hg}$  and  $P_B^\circ = 200 \text{ mm Hg}$ ]  
(A) 0.4 (B) 0.8 (C) 0.25 (D) none of these
- At a given temperature, total vapour pressure in Torr of a mixture of volatile components A and B is given by  
$$P_{\text{Total}} = 120 - 75 X_B$$
hence, vapour pressure of pure A and B respectively (in Torr) are  
(A) 120, 75 (B) 120, 195 (C) 120, 45 (D) 75, 45
- Two liquids A & B form an ideal solution. What is the vapour pressure of solution containing 2 moles of A and 3 moles of B at 300 K? [Given : At 300 K, Vapour pr. of pure liquid A ( $P_A^\circ$ ) = 100 torr, Vapour pr. of pure liquid B ( $P_B^\circ$ ) = 300 torr ]  
(A) 200 torr (B) 140 torr (C) 180 torr (D) None of these
- If Raoult's law is obeyed, the vapour pressure of the solvent in a solution is directly proportional to  
(A) Mole fraction of the solvent  
(B) Mole fraction of the solute  
(C) Mole fraction of the solvent and solute  
(D) The volume of the solution
- 1 mole of heptane (V. P. = 92 mm of Hg) was mixed with 4 moles of octane (V. P. = 31 mm of Hg). The vapour pressure of resulting ideal solution is :  
(A) 46.2 mm of Hg (B) 40.0 mm of Hg  
(C) 43.2 mm of Hg (D) 38.4 mm of Hg
- Mole fraction of A vapours above solution in mixture of A and B ( $X_A = 0.4$ ) will be :-  
( $P_A^\circ = 100 \text{ mm}$ ,  $P_B^\circ = 200 \text{ mm}$ )  
(A) 0.4 (B) 0.8 (C) 0.25 (D) None
- The vapour pressure of a pure liquid 'A' is 70 torr at  $27^\circ C$ . It forms an ideal solution with another liquid B. The mole fraction of B is 0.2 and total vapour pressure of the solution is 84 torr at  $27^\circ C$ . The vapour pressure of pure liquid B at  $27^\circ C$  is  
(A) 14 (B) 56 (C) 140 (D) 70
- At  $88^\circ C$  benzene has a vapour pressure of 900 torr and toluene has a vapour pressure of 360 torr. What is the mole fraction of benzene in the mixture with toluene that will boil at  $88^\circ C$  at 1 atm. pressure, benzene - toluene form an ideal solution:  
(A) 0.416 (B) 0.588 (C) 0.688 (D) 0.740

10. The exact mathematical expression of Raoult's law is ( $n$  = moles of solute ;  $N$  = moles of solvent)
- (A)  $\frac{P^0 - P_s}{P^0} = \frac{n}{N}$  (B)  $\frac{P^0 - P_s}{P^0} = \frac{N}{n}$  (C)  $\frac{P^0 - P_s}{P_s} = \frac{n}{N}$  (D)  $\frac{P^0 - P_s}{P^0} = n \times N$
11. The vapour pressure of a solvent decreased by 10 mm of Hg when a non-volatile solute was added to the solvent. The mole fraction of solute in solution is 0.2, what would be mole fraction of the solvent if decrease in vapour pressure is 20 mm of Hg
- (A) 0.2 (B) 0.4 (C) 0.6 (D) 0.8
12. The vapour pressure of a solution having solid as solute and liquid as solvent is :
- (A) Directly proportional to mole fraction of the solvent  
(B) Inversely proportional to mole fraction of the solvent  
(C) Directly proportional to mole fraction of the solute  
(D) Inversely proportional to mole fraction of the solute
13. One mole of non volatile solute is dissolved in two moles of water. The vapour pressure of the solution relative to that of water is
- (A)  $\frac{2}{3}$  (B)  $\frac{1}{3}$  (C)  $\frac{1}{2}$  (D)  $\frac{3}{2}$
14. The vapour pressure of pure A is 10 torr and at the same temperature when 1 g of B is dissolved in 20 gm of A, its vapour pressure is reduced to 9.0 torr. If the molecular mass of A is 200 amu, then the molecular mass of B is :
- (A) 100 amu (B) 90 amu (C) 75 amu (D) 120 amu
15. The vapour pressure of a pure liquid solvent (X) is decreased to 0.60 atm. from 0.80 atm on addition of a non volatile substance (Y). The mole fraction of (Y) in the solution is:-
- (A) 0.20 (B) 0.25 (C) 0.5 (D) 0.75
16. Among the following, that does not form an ideal solution is :
- (A)  $C_6H_6$  and  $C_6H_5CH_3$  (B)  $C_2H_5Cl$  and  $C_6H_5OH$   
(C)  $C_6H_5Cl$  and  $C_6H_5Br$  (D)  $C_2H_5Br$  and  $C_2H_5I$
17. Colligative properties of the solution depend upon
- (A) Nature of the solution (B) Nature of the solvent  
(C) Number of solute particles (D) Number of moles of solvent
18. Elevation of boiling point of 1 molar aqueous glucose solution (density = 1.2 g/ml) is
- (A)  $K_b$  (B)  $1.20 K_b$  (C)  $1.02 K_b$  (D)  $0.98 K_b$
19. When common salt is dissolved in water
- (A) Melting point of the solution increases  
(B) Boiling point of the solution increases  
(C) Boiling point of the solution decreases  
(D) Both Melting point and Boiling point is decreases
20. What should be the freezing point of aqueous solution containing 17 gm of  $C_2H_5OH$  in 1000 gm of water (water  $K_f = 1.86 \text{ deg} - \text{kg mol}^{-1}$ )
- (A)  $-0.69^\circ\text{C}$  (B)  $-0.34^\circ\text{C}$  (C)  $0.0^\circ\text{C}$  (D)  $0.34^\circ\text{C}$



21. If mole fraction of the solvent in solution decreases then :  
 (A) Vapour pressure of solution increases  
 (B) B. P. decreases  
 (C) Osmotic pressure increases  
 (D) All are correct
22. 5% (w/v) solution of sucrose is isotonic with 1% (w/v) solution of a compound 'A' then the molecular weight of compound 'A' is -  
 (A) 32.4 (B) 68.4 (C) 121.6 (D) 34.2
23. Osmotic pressure of a sugar solution at 24°C is 2.5 atmosphere. The concentration of the solution in mole per litre is :  
 (A) 10.25 (B) 1.025 (C) 1025 (D) 0.1025
24. A solution containing 4 g of a non volatile organic solute per 100 ml was found to have an osmotic pressure equal to 500 cm of mercury at 27°C. The molecular weight of solute is :  
 (A) 14.97 (B) 149.7 (C) 1697 (D) 1.497
25. If a 6.84% (wt. / vol.) solution of cane-sugar (mol. wt. 342) is isotonic with 1.52% (wt./vol.) solution of thiocarbamide, then the molecular weight of thiocarbamide is :  
 (A) 152 (B) 76 (C) 60 (D) 180
26. Which of the following aqueous solution will show maximum vapour pressure at 300 K?  
 (A) 1 M NaCl (B) 1 M CaCl<sub>2</sub> (C) 1 M AlCl<sub>3</sub> (D) 1 M C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>
27. The correct relationship between the boiling points of very dilute solution of AlCl<sub>3</sub> (T<sub>1</sub>K) and CaCl<sub>2</sub> (T<sub>2</sub>K) having the same molar concentration is  
 (A) T<sub>1</sub> = T<sub>2</sub> (B) T<sub>1</sub> > T<sub>2</sub> (C) T<sub>2</sub> > T<sub>1</sub> (D) T<sub>2</sub> ≤ T<sub>1</sub>
28. 1.0 molal aqueous solution of an electrolyte A<sub>2</sub>B<sub>3</sub> is 60% ionised. The boiling point of the solution at 1 atm is (K<sub>b</sub>(H<sub>2</sub>O) = 0.52 K kg mol<sup>-1</sup>)  
 (A) 274.76 K (B) 377 K (C) 376.4 K (D) 374.76 K
29. The freezing point depression of a 0.1 M a solution of weak acid (HX) is -0.20°C. What is the value of equilibrium constant for the reaction?  

$$\text{HX (aq)} \rightleftharpoons \text{H}^+(\text{aq}) + \text{X}^-(\text{aq})$$
  
 [Given : K<sub>f</sub> for water = 1.8 kg mol<sup>-1</sup> K. & Molality = Molarity ]  
 (A) 1.46 × 10<sup>-4</sup> (B) 1.35 × 10<sup>-3</sup> (C) 1.21 × 10<sup>-2</sup> (D) 1.35 × 10<sup>-4</sup>
30. The Vant Hoff factor (i) for a dilute solution of K<sub>3</sub>[Fe(CN)<sub>6</sub>] is (Assuming 100% ionsation) :  
 (A) 10 (B) 4 (C) 5 (D) 0.25
31. The substance A when dissolved in solvent B shows the molecular mass corresponding to A<sub>3</sub>. The vant Hoff's factor will be -  
 (A) 1 (B) 2 (C) 3 (D) 1/3

32. The value of observed and calculated molecular weight of silver nitrate are 92.64 and 170 respectively. The degree of dissociation of silver nitrate is :  
 (A) 60% (B) 83.5 % (C) 46.7% (D) 60.23%
33. The freezing point of 1 molal NaCl solution assuming NaCl to be 100% dissociated in water is : ( $K_f = 1.86 \text{ K Molality}^{-1}$ )  
 (A)  $-1.86^\circ\text{C}$  (B)  $-3.72^\circ\text{C}$  (C)  $+1.86^\circ\text{C}$  (D)  $+3.72^\circ\text{C}$
34. What is the freezing point of a solution containing 8.1 gm. of HBr in 100gm. water assuming the acid to be 90% ionised ( $K_f$  for water =  $1.86 \text{ K molality}^{-1}$ ) :-  
 (A)  $0.85^\circ\text{C}$  (B)  $-3.53^\circ\text{C}$  (C)  $0^\circ\text{C}$  (D)  $-0.35^\circ\text{C}$
35. If a ground water contains  $\text{H}_2\text{S}$  at concentration of 2 mg/l, determine the pressure of  $\text{H}_2\text{S}$  in head space of a closed tank containing the ground water at  $20^\circ\text{C}$ . Given that for  $\text{H}_2\text{S}$ , Henry's constant is equal to  $6.8 \times 10^3 \text{ bar}$  at  $20^\circ\text{C}$ .  
 (A) 720 Pa (B)  $77 \times 10^2 \text{ Pa}$  (C) 553 Pa (D)  $55 \times 10^2 \text{ Pa}$
36. A pressure cooker reduces cooking time for food because -  
 (A) The higher pressure inside the cooker crushes the food material  
 (B) Cooking involves chemical changes helped by a rise in temperature  
 (C) Heat is more evenly distributed in the cooking space  
 (D) Boiling point of water involved in cooking is increased

## EXERCISE # O-II

## Single correct :

- An ideal solution was obtained by mixing (MeOH) methanol and (EtOH) ethanol. If the partial vapour pressure of methanol and ethanol are 2.619 K Pa and 4.556 K Pa respectively, the composition of vapour (in terms of mole fraction) will be -  
 (A) 0.635 MeOH, 0.365 EtOH (B) 0.365 MeOH, 0.635 EtOH  
 (C) 0.574 MeOH, 0.326 EtOH (D) 0.173 MeOH, 0.827 EtOH
- Molar volume of liquid A ( $d = 0.8 \text{ gm/ml}$ ) increase by factor of 2000 when it vapourises at 200K. Vapour pressure of liquid A at 200K is [ $R = 0.08 \text{ L-atm/mol-K}$ ]  
 (Molar mass of A = 80g/mol)  
 (A) 0.4 atm (B) 8 atm (C) 0.8 atm (D) 0.08 atm
- Assuming each salt to be 90 % dissociated, which of the following will have highest boiling point?  
 (A) Decimolar  $\text{Al}_2(\text{SO}_4)_3$   
 (B) Decimolar  $\text{BaCl}_2$   
 (C) Decimolar  $\text{Na}_2\text{SO}_4$   
 (D) A solution obtained by mixing equal volumes of (B) and (C)
- The vapour pressure of a saturated solution of sparingly soluble salt ( $\text{XCl}_3$ ) was 17.20 mm Hg at  $27^\circ\text{C}$ . If the vapour pressure of pure  $\text{H}_2\text{O}$  is 17.25 mm Hg at 300 K, what is the solubility of sparingly soluble salt  $\text{XCl}_3$  in mole/Litre.  
 (A)  $4.04 \times 10^{-2}$  (B)  $8.08 \times 10^{-2}$  (C)  $2.02 \times 10^{-2}$  (D)  $4.04 \times 10^{-3}$
- A solution has a 1 : 4 mole ratio of pentane to hexane. The vapour pressures of the pure hydrocarbons at  $20^\circ\text{C}$  are 440 mmHg for pentane and 120 mmHg for hexane. The mole fraction of pentane in the vapour phase would be :-  
 (A) 0.200 (B) 0.478 (C) 0.549 (D) 0.786
- For which of the following vant' Hoff's factor is not correctly matched -  

| Salt                                                 | Degree of dissociation ( $\alpha$ ) | $i$  |
|------------------------------------------------------|-------------------------------------|------|
| (A) $\text{Na}_2\text{SO}_4$                         | 50 %                                | 2    |
| (B) $\text{K}_3[\text{Fe}(\text{CN})_6]$             | 75%                                 | 3.25 |
| (C) $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$            | 80 %                                | 1.8  |
| (D) $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$ | 90 %                                | 2.8  |
- In the depression of freezing point experiment, it is found that  
 (I) The vapour pressure of the solution is less than that of pure solvent.  
 (II) The vapour pressure of the solution is more than that of pure solvent.  
 (III) Only solute molecules solidify at the freezing point.  
 (IV) Only solvent molecules solidify at the freezing point.  
 (A) I, II (B) II, III (C) I, IV (D) I, II, III

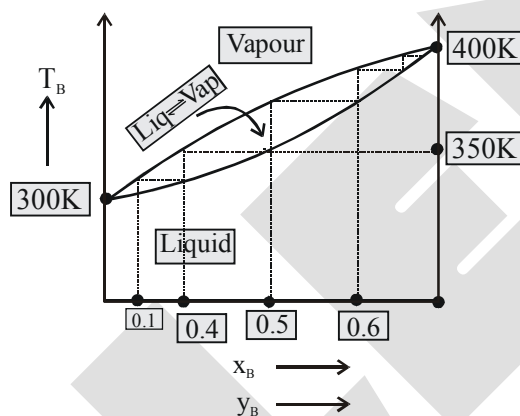
8. **Statement-1** : Addition of ethylene glycol (non-volatile) to water lowers the freezing point of water hence used as antifreeze.

**Statement-2** : Addition of any substance to water lowers its freezing point of water.

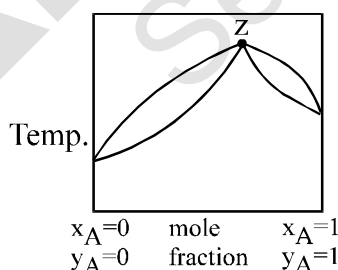
- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

**More than one may be correct**

9. For an ideal solution having two liquid A ( $P_A^0$ ) and liquid B ( $P_B^0$ ) boiling point versus composition graph is given below, then select incorrect statement (s) :



- (A) B is less volatile than A  
 (B) If mole percent of A in liquid phase is 40% then mole percent of A in vapour phase is 50%  
 (C) If mole percent of B in liquid phase is 10% then mole percent of B in vapour phase is 40%  
 (D) If the mole percent of A in solution is 50% then its boiling point is 350K
10. A liquid mixture having composition corresponding to point z in the figure shown is subjected to distillation at constant pressure.



Which of the following statement is correct about the process

- (A) The composition of distillate differs from the mixture  
 (B) The boiling point goes on changing  
 (C) The mixture has lowest vapour pressure than for any other composition.  
 (D) Composition of an azeotrope alters on changing the external pressure.

11. Which of the following is correct for a non-ideal solution of liquids A and B, showing negative deviation?

(A)  $\Delta H_{\text{mix}} = -ve$

(B)  $\Delta V_{\text{mix}} = -ve$

(C)  $\Delta S_{\text{mix}} = +ve$

(D)  $\Delta G_{\text{mix}} = -ve$

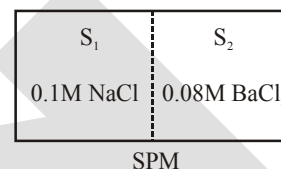
12. Two solutions  $S_1$  and  $S_2$  containing 0.1M NaCl(aq.) and 0.08M BaCl<sub>2</sub>(aq.) are separated by semipermeable membrane. Which among the following statement(s) is/are correct -

(A)  $S_1$  and  $S_2$  are isotonic

(B)  $S_1$  is hypertonic and  $S_2$  is hypotonic

(C)  $S_1$  is hypotonic and  $S_2$  is hypertonic

(D) Osmosis will take place to from  $S_1$  to  $S_2$



13. For an ideal binary liquid solution with  $P_A^\circ > P_B^\circ$ , which relation between  $X_A$  (mole fraction of A in liquid phase) and  $Y_A$  (mole fraction of A in vapour phase) is correct?

(A)  $Y_A < Y_B$

(B)  $X_A > X_B$

(C)  $\frac{Y_A}{Y_B} > \frac{X_A}{X_B}$

(D)  $\frac{Y_A}{Y_B} < \frac{X_A}{X_B}$

14. Which of the following plots represents an ideal binary mixture?

(A) Plot of  $P_{\text{total}}$  v/s  $1/X_B$  is linear ( $X_B$  = mole fraction of 'B' in liquid phase).

(B) Plot of  $P_{\text{total}}$  v/s  $Y_A$  is linear ( $Y_B$  = mole fraction of 'A' in vapour phase)

(C) Plot of  $\frac{1}{P_{\text{total}}}$  v/s  $Y_A$  is linear

(D) Plot of  $\frac{1}{P_{\text{total}}}$  v/s  $Y_B$  is non linear

### Paragraph for Q.15 to Q.17

An ideal solution is obtained by mixing a non-volatile solute B with a volatile solvent A (molar mass = 60). If the mass ratio of A : B in solution is 10 : 1 and vapour pressure of pure A is 400 mm and vapour pressure decreases by 4% on forming the above solution at 300K.

15. The mole fraction of solute in the solution is -

(A) 0.96

(B) 0.04

(C) 0.16

(D) 0.84

16. The molality the solution is -

(A) 1

(B)  $\frac{36}{25}$

(C)  $\frac{25}{36}$

(D)  $\frac{36}{25}$

17. The molar mass of B in the solution is -

(A) 1440

(B) 14400

(C) 4

(D) 144

Table type question :

| Column-I                   | Column-II            | Column-III                         |
|----------------------------|----------------------|------------------------------------|
| (1) $C_6H_6 + C_6H_5-CH_3$ | (a) $\Delta H = 0$   | (P) $\Delta G = -ve$               |
| (2) $CHCl_3 + CH_3COCH_3$  | (b) $\Delta H = +ve$ | (Q) Form minimum boiling azeotrope |
| (3) $CCl_4 + CH_3COCH_3$   | (c) $\Delta H = -ve$ | (R) Form maximum boiling azeotrope |
| (4) $C_2H_5OH + H_2O$      | (d) $\Delta S = +ve$ | (S) No azeotrope                   |

18. Select the correct match -

- (A) 1, a, R (B) 2, b, P (C) 3, b, Q (D) 4, d, R

19. Select the correct match -

- (A) 1, d, S (B) 3, b, S (C) 2, b, S (D) 4, c, P

20. Select the incorrect match -

- (A) 1, d, P (B) 2, c, R (C) 3, d, S (D) 3, b, P

Match the column :

| 21. Column-I<br>(Colligative properties)                                                                                                   | Column-II<br>(Aqueous solution)<br>(Assume $m = M$ ) |
|--------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------|
| (A) $\Delta T_f = 0.3 \times K_f$                                                                                                          | (P) 0.1 m - $Ca(NO_3)_2$                             |
| (B) $\Delta T_b = 0.28 \times K_b$                                                                                                         | (Q) 0.14 m - NaBr                                    |
| (C) $\pi = 0.19 \times RT$                                                                                                                 | (R) 0.1 m - $MgCl_2$ ( $\alpha = 0.9$ )              |
| (D) $\frac{P^0 - P}{P^0} = \frac{\left(\frac{\Delta T_f}{K_f}\right)}{\left(\frac{1000}{18}\right) + \left(\frac{\Delta T_f}{K_f}\right)}$ | (S) 0.28 m - Urea                                    |
|                                                                                                                                            | (T) 0.1 m - HA (monobasic acid, $K_a = 0.81$ )       |

## EXERCISE # (J-MAIN)

- The degree of dissociation ( $i$ ) of a weak electrolyte,  $A_xB_y$  is related to van't Hoff factor ( $i$ ) by the expression :- [AIEEE-2011]  
 (1)  $\alpha = \frac{x+y-1}{i-1}$       (2)  $\alpha = \frac{x+y+1}{i-1}$       (3)  $\alpha = \frac{i-1}{(x+y-1)}$       (4)  $\alpha = \frac{i-1}{x+y+1}$
- $K_f$  for water is  $1.86 \text{ K kg mol}^{-1}$ . If your automobile radiator holds  $1.0 \text{ kg}$  of water, how many grams of ethylene glycol ( $C_2H_6O_2$ ) must you add to get the freezing point of the solution lowered to  $-2.8^\circ\text{C}$  ? [AIEEE-2012]  
 (1)  $27 \text{ g}$       (2)  $72 \text{ g}$       (3)  $93 \text{ g}$       (4)  $39 \text{ g}$
- A solution containing  $0.85 \text{ g}$  of  $ZnCl_2$  in  $125.0 \text{ g}$  of water freezes at  $-0.23^\circ\text{C}$ . The apparent degree of dissociation of the salt is : [JEE (MAIN)-2012 ONLINE]  
 ( $k_f$  for water =  $1.86 \text{ K kg mol}^{-1}$ , atomic mass ;  $Zn = 65.3$  and  $Cl = 35.5$ )  
 (1)  $1.36\%$       (2)  $2.47\%$       (3)  $73.5\%$       (4)  $7.35\%$
- Liquids A and B form an ideal solution. At  $30^\circ\text{C}$ , the total vapour pressure of a solution containing  $1 \text{ mol}$  of A and  $2 \text{ moles}$  of B is  $250 \text{ mm Hg}$ . The total vapour pressure becomes  $300 \text{ mm Hg}$  when  $1 \text{ more mol}$  of A is added to the first solution. The vapour pressures of pure A and B at the same temperature are [JEE (MAIN)-2012 ONLINE]  
 (1)  $450, 150 \text{ mm Hg}$       (2)  $250, 300 \text{ mm Hg}$       (3)  $125, 150 \text{ mm Hg}$       (4)  $150, 450 \text{ mm Hg}$
- The freezing point of a  $1.00 \text{ m}$  aqueous solution of HF is found to be  $-1.91^\circ\text{C}$ . The freezing point constant of water,  $K_f$ , is  $1.86 \text{ K kg mol}^{-1}$ . The percentage dissociation of HF at this concentration is [JEE (MAIN)-2012 ONLINE]  
 (1)  $2.7\%$       (2)  $30\%$       (3)  $10\%$       (4)  $5.2\%$
- How many grams of methyl alcohol should be added to  $10 \text{ litre}$  tank of water to prevent its freezing at  $268 \text{ K}$  ? [JEE (MAIN)-2013 ONLINE]  
 ( $K_f$  for water is  $1.86 \text{ K kg mol}^{-1}$ )  
 (1)  $899.04 \text{ g}$       (2)  $786 \text{ g}$       (3)  $860 \text{ g}$       (4)  $880.07 \text{ g}$
- Vapour pressure of pure benzene is  $119 \text{ torr}$  and that of toluene is  $37.0 \text{ torr}$  at the same temperature. Mole fraction of toluene in vapour phase which is in equilibrium with a solution of benzene and toluene having a mole fraction of toluene  $0.50$ , will be : [JEE (MAIN)-2013 ONLINE]  
 (1)  $0.137$       (2)  $0.205$       (3)  $0.237$       (4)  $0.435$
- A molecule M associates in a given solvent according to the equation  $M \rightleftharpoons (M)_n$ . For a certain concentration of M, the van't Hoff factor was found to be  $0.9$  and the fraction of associated molecules was  $0.2$ . The value of  $n$  is : [JEE (MAIN)-2013 ONLINE]  
 (1)  $2$       (2)  $4$       (3)  $5$       (4)  $3$
- $12 \text{ g}$  of a nonvolatile solute dissolved in  $108 \text{ g}$  of water produces the relative lowering of vapour pressure of  $0.1$ . The molecular mass of the solute is : [JEE (MAIN)-2013 ONLINE]  
 (1)  $60$       (2)  $80$       (3)  $40$       (4)  $20$
- The molarity of a solution obtained by mixing  $750 \text{ mL}$  of  $0.5 \text{ (M) HCl}$  with  $250 \text{ mL}$  of  $2 \text{ (M) HCl}$  will be :- [JEE (MAIN)-2013]  
 (1)  $0.875 \text{ M}$       (2)  $1.00 \text{ M}$       (3)  $1.75 \text{ M}$       (4)  $0.975 \text{ M}$

11. The observed osmotic pressure for a 0.10 M solution of  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$  at  $25^\circ\text{C}$  is 10.8 atm. The expected and experimental (observed) values of Van't Hoff factor (i) will be respectively :  
 ( $R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$ ) [JEE (MAIN)-2014 ONLINE]  
 (1) 3 and 5.42 (2) 5 and 3.42 (3) 4 and 4.00 (4) 5 and 4.42
12. For an ideal Solution of two components A and B, which of the following is true ?  
 (1)  $\Delta H_{\text{mixing}} < 0$  (zero) [JEE(MAIN)-2014 ONLINE]  
 (2) A – A, B – B and A – B interactions are identical  
 (3) A – B interaction is stronger than A – A and B – B interactions  
 (4)  $\Delta H_{\text{mixing}} > 0$  (zero)
13. Consider separate solution of 0.500 M  $\text{C}_2\text{H}_5\text{OH}(\text{aq})$ , 0.100 M  $\text{Mg}_3(\text{PO}_4)_2(\text{aq})$ , 0.250 M  $\text{KBr}(\text{aq})$  and 0.125 M  $\text{Na}_3\text{PO}_4(\text{aq})$  at  $25^\circ\text{C}$ . Which statement is true about these solutions, assuming all salts to be strong electrolytes ? [JEE (MAIN)-2014]  
 (1) 0.125 M  $\text{Na}_3\text{PO}_4(\text{aq})$  has the highest osmotic pressure.  
 (2) 0.500 M  $\text{C}_2\text{H}_5\text{OH}(\text{aq})$  has the highest osmotic pressure.  
 (3) They all have the same osmotic pressure.  
 (4) 0.100 M  $\text{Mg}_3(\text{PO}_4)_2(\text{aq})$  has the highest osmotic pressure.
14. Determination of the molar mass of acetic acid in benzene using freezing point depression is affected by :  
 [JEE (MAIN)-2015 ONLINE]  
 (1) association (2) dissociation (3) complex formation (4) partial ionization
15. A solution at  $20^\circ\text{C}$  is composed of 1.5 mol of benzene and 3.5 mol of toluene. If the vapour pressure of pure benzene and pure toluene at this temperature are 74.7 torr and 22.3 torr, respectively, then the total vapour pressure of the solution and the benzene mole fraction in equilibrium with it will be, respectively :  
 [JEE (MAIN)-2015 ONLINE]  
 (1) 38.0 torr and 0.589 (2) 30.5 torr and 0.389  
 (3) 35.8 torr and 0.280 (4) 35.0 torr and 0.480
16. The vapour pressure of acetone at  $20^\circ\text{C}$  is 185 torr. When 1.2 g of non-volatile substance was dissolved in 100 g of acetone at  $20^\circ\text{C}$ , its vapour pressure was 183 torr. The molar mass ( $\text{g mol}^{-1}$ ) of the substance is :  
 [JEE (MAIN)-2015]  
 (1) 128 (2) 488 (3) 32 (4) 64
17. An aqueous solution of a salt  $\text{MX}_2$  at certain temperature has a van't Hoff factor of 2. The degree of dissociation for this solution of the salt is :  
 [JEE (MAIN)-2016-ONLINE]  
 (1) 0.50 (2) 0.80 (3) 0.67 (4) 0.33
18. The solubility of  $\text{N}_2$  in water at 300 K and 500 torr partial pressure is 0.01  $\text{g L}^{-1}$ . The solubility (in  $\text{g L}^{-1}$ ) at 750 torr partial pressure is :  
 [JEE (MAIN)-2016-ONLINE]  
 (1) 0.02 (2) 0.005 (3) 0.015 (4) 0.0075
19. 18 g glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) is added to 178.2 g at  $100^\circ\text{C}$  water. The vapour pressure of water (in torr) for this aqueous solution is :  
 [JEE (MAIN)-2016]  
 (1) 759.0 (2) 7.6 (3) 76.0 (4) 752.4



20. The freezing point of benzene decreases by  $0.45^{\circ}\text{C}$  when 0.2 g of acetic acid is added to 20 g of benzene. If acetic acid associates to form a dimer in benzene, percentage association of acetic acid in benzene will be :- ( $K_f$  for benzene =  $5.12 \text{ K kg mol}^{-1}$ ) [JEE (MAIN)-2017]
- (1) 64.6% (2) 80.4% (3) 74.6% (4) 94.6%
21. 5 g of  $\text{Na}_2\text{SO}_4$  was dissolved in x g of  $\text{H}_2\text{O}$ . The change in freezing point was found to be  $3.82^{\circ}\text{C}$ . If  $\text{Na}_2\text{SO}_4$  is 81.5% ionised, the value of x ( $K_f$  for water =  $1.86^{\circ}\text{C kg mol}^{-1}$ ) is approximately. (Molar mass of S =  $32 \text{ g mol}^{-1}$  and that of Na =  $23 \text{ g mol}^{-1}$ ) [JEE (MAIN-2017-ONLINE)]
- (1) 45 g (2) 65 g (3) 15 g (4) 25 g
22. A solution is prepared by mixing 8.5 g of  $\text{CH}_2\text{Cl}_2$  and 11.95 g of  $\text{CHCl}_3$ . If vapour pressure of  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$  at 298 K are 415 and 200 mmHg respectively, the mole fraction of  $\text{CHCl}_3$  in vapour form is: (Molar mass of Cl =  $35.5 \text{ g mol}^{-1}$ ) [JEE (MAIN-2017-ONLINE)]
- (1) 0.486 (2) 0.325 (3) 0.162 (4) 0.675
23. For 1 molal aqueous solution of the following compounds, which one will show the highest freezing point ? [JEE (MAIN)-2018]
- (1)  $[\text{Co}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$   
 (2)  $[\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$   
 (3)  $[\text{Co}(\text{H}_2\text{O})_3\text{Cl}_3] \cdot 3\text{H}_2\text{O}$   
 (4)  $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_3$
24. Two 5 molal solutions are prepared by dissolving a non-electrolyte non-volatile solute separately in the solvents X and Y. The molecular weights of the solvents are  $M_x$  and  $M_y$ , respectively where  $M_x = \frac{3}{4} M_y$ . The relative lowering of vapour pressure of the solution in X is "m" times that of the solution in Y. Given that the number of moles of solute is very small in comparison to that of solvent, the value of "m" is - [JEE (MAIN-2018-ONLINE)]
- (1)  $\frac{3}{4}$  (2)  $\frac{4}{3}$  (3)  $\frac{1}{2}$  (4)  $\frac{1}{4}$
25. The mass of a non-volatile, non-electrolyte solute (molar mass =  $50 \text{ g mol}^{-1}$ ) needed to be dissolved in 114 g octane to reduce its vapour pressure by 75%, is :- [JEE (MAIN-2018-ONLINE)]
- (1) 50 g (2) 37.5 g (3) 75 g (4) 150 g

EXERCISE # (J-ADVANCED)

- To 500 cm<sup>3</sup> of water,  $3 \times 10^{-3}$  kg of acetic acid is added. If 23% of acetic acid is dissociated, what will be the depression in freezing point?  $K_f$  and density of water are 1.86 K kg<sup>-1</sup> mol<sup>-1</sup> and 0.997 g cm<sup>-3</sup> respectively. [JEE 2000]
- The vapour pressure of two miscible liquids (A) and (B) are 300 and 500 mm of Hg respectively. In a flask 10 mole of (A) is mixed with 12 mole of (B). However, as soon as (B) is added, (A) starts polymerising into a completely insoluble solid. The polymerisation follows first-order kinetics. After 100 minute, 0.525 mole of a solute is dissolved which arrests the polymerisation completely. The final vapour pressure of the solution is 400 mm of Hg. Estimate the rate constant of the polymerisation reaction. Assume negligible volume change on mixing and polymerisation and ideal behaviour for the final solution. [JEE 2001]
- Match the boiling point with  $K_b$  for x, y and z, if molecular weight of x, y and z are same. [JEE 2003]

|   | b.pt. | $K_b$ |
|---|-------|-------|
| x | 100   | 0.68  |
| y | 27    | 0.53  |
| z | 253   | 0.98  |
- During depression of freezing point in a solution, the following are in equilibrium [JEE 2003]

|                                  |                                 |
|----------------------------------|---------------------------------|
| (A) liquid solvent-solid solvent | (B) liquid solvent-solid solute |
| (C) liquid solute-solid solute   | (D) liquid solute-solid solvent |
- 1.22 g of benzoic acid is dissolved in (i) 100 g acetone ( $K_b$  for acetone = 1.7) and (ii) 100 g benzene ( $K_b$  for benzene = 2.6). The elevation in boiling points  $T_b$  is 0.17°C and 0.13°C respectively.
  - What are the molecular weights of benzoic acid in both the solutions?
  - What do you deduce out of it in terms of structure of benzoic acid? [JEE 2004]
- A 0.004 M solution of  $\text{Na}_2\text{SO}_4$  is isotonic with a 0.010 M solution of glucose at same temperature. The apparent degree of dissociation of  $\text{Na}_2\text{SO}_4$  is

|         |         |         |         |
|---------|---------|---------|---------|
| (A) 25% | (B) 50% | (C) 75% | (D) 85% |
|---------|---------|---------|---------|

[JEE 2004]
- The elevation in boiling point, when 13.44 g of freshly prepared  $\text{CuCl}_2$  are added to one kilogram of water, is [Some useful data,  $K_b$  ( $\text{H}_2\text{O}$ ) = 0.52 K kg mol<sup>-1</sup>, mol. wt. of  $\text{CuCl}_2$  = 134.4 gm]

|          |         |          |          |
|----------|---------|----------|----------|
| (A) 0.05 | (B) 0.1 | (C) 0.16 | (D) 0.21 |
|----------|---------|----------|----------|

[JEE 2005]
- 72.5 g of phenol is dissolved in 1 kg of a solvent ( $k_f$  = 14) which leads to dimerization of phenol and freezing point is lowered by 7 kelvin. What percent of total phenol is present in dimeric form? [JEE 2006]
- When 20 g of naphtholic acid ( $\text{C}_{11}\text{H}_8\text{O}_2$ ) is dissolved in 50 g of benzene ( $K_f$  = 1.72 K kg mol<sup>-1</sup>), a freezing point depression of 2 K is observed. The van't Hoff factor ( $i$ ) is [JEE 2007]

|         |       |       |       |
|---------|-------|-------|-------|
| (A) 0.5 | (B) 1 | (C) 2 | (D) 3 |
|---------|-------|-------|-------|

**Paragraph for Question No. Q.10 to Q.12**

Properties such as boiling point, freezing point and vapour pressure of a pure solvent change when solute molecules are added to get homogeneous solution. These are called colligative properties. Applications of colligative properties are very useful in day-to-day life. One of its examples is the use of ethylene glycol and water mixture as anti-freezing liquid in the radiator of automobiles.

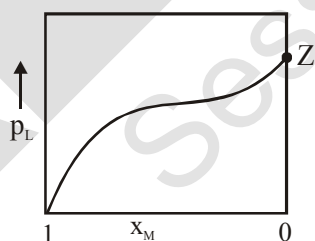
A solution **M** is prepared by mixing ethanol and water. The mole fraction of ethanol in the mixture is 0.9.

- Given :
- Freezing point depression constant of water ( $K_f^{\text{water}}$ ) =  $1.86 \text{ K kg mol}^{-1}$
  - Freezing point depression constant of ethanol ( $K_f^{\text{ethanol}}$ ) =  $2.0 \text{ K kg mol}^{-1}$
  - Boiling point elevation constant of water ( $K_b^{\text{water}}$ ) =  $0.52 \text{ K kg mol}^{-1}$
  - Boiling point elevation constant of ethanol ( $K_b^{\text{ethanol}}$ ) =  $1.2 \text{ K kg mol}^{-1}$
  - Standard freezing point of water =  $273 \text{ K}$
  - Standard freezing point of ethanol =  $155.7 \text{ K}$
  - Standard boiling point of water =  $373 \text{ K}$
  - Standard boiling point of ethanol =  $351.5 \text{ K}$
  - Vapour pressure of pure water =  $32.8 \text{ mm Hg}$
  - Vapour pressure of pure ethanol =  $40 \text{ mm Hg}$
  - Molecular weight of water =  $18 \text{ g mol}^{-1}$
  - Molecular weight of ethanol =  $46 \text{ g mol}^{-1}$

In answering the following questions, consider the solutions to be ideal dilute solutions and solutes to be non-volatile and non-dissociative.

10. The freezing point of the solution **M** is [JEE 2008]  
 (A) 268.7 K      (B) 268.5 K      (C) 234.2 K      (D) 150.9 K
11. The vapour pressure of the solution **M** is [JEE 2008]  
 (A) 39.3 mm Hg      (B) 36.0 mm Hg      (C) 29.5 mm Hg      (D) 28.8 mm Hg
12. Water is added to the solution **M** such that the mole fraction of water in the solution becomes 0.9. The boiling point of this solution is [JEE 2008]  
 (A) 380.4 K      (B) 376.2 K      (C) 375.5 K      (D) 354.7 K
13. The Henry's law constant for the solubility of  $\text{N}_2$  gas in water at 298 K is  $1.0 \times 10^5 \text{ atm}$ . The mole fraction of  $\text{N}_2$  in air is 0.8. The number of moles of  $\text{N}_2$  from air dissolved in 10 moles of water at 298 K and 5 atm pressure is- [JEE 2009]  
 (A)  $4.0 \times 10^{-4}$       (B)  $4.0 \times 10^{-5}$       (C)  $5.0 \times 10^{-4}$       (D)  $4.0 \times 10^{-5}$
14. For a dilute solution containing 2.5 g of a non-volatile non-electrolyte solute in 100 g of water, the elevation in boiling point at 1 atm pressure is  $2^\circ\text{C}$ . Assuming concentration of solute is much lower than the concentration of solvent, the vapour pressure (mm of Hg) of the solution is- (take  $K_b = 0.76 \text{ K kg mol}^{-1}$ ) [JEE 2011]  
 (A) 724      (B) 740      (C) 736      (D) 718

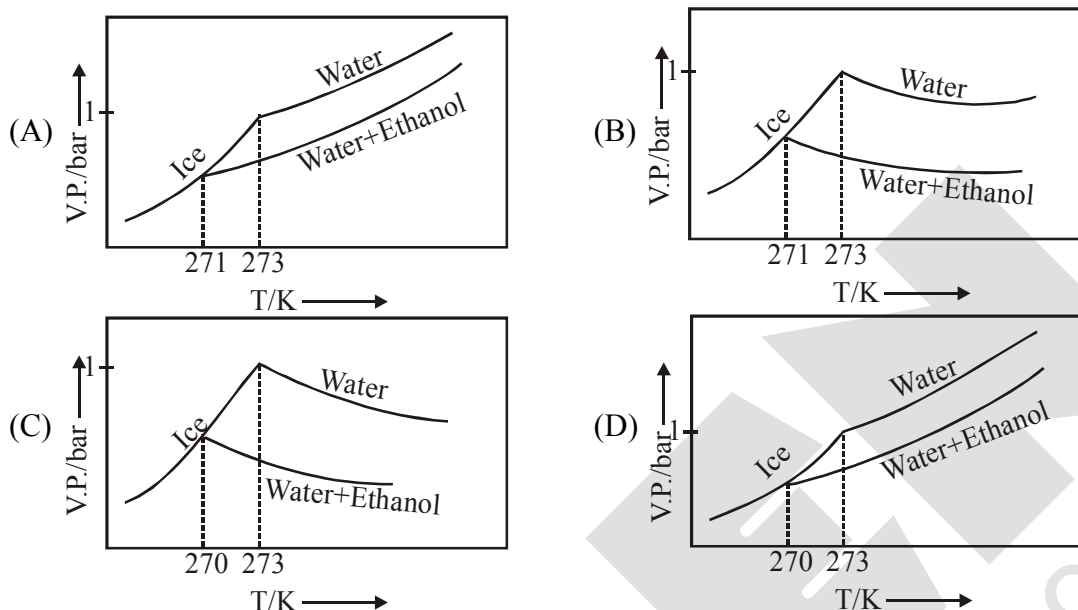
15. The freezing point (in  $^{\circ}\text{C}$ ) of a solution containing 0.1 g of  $\text{K}_3[\text{Fe}(\text{CN})_6]$  (Mol. Wt. 329) in 100 g of water ( $K_f = 1.86 \text{ K kg mol}^{-1}$ ) is - [JEE 2011]  
 (A)  $-2.3 \times 10^{-2}$  (B)  $-5.7 \times 10^{-2}$  (C)  $-5.7 \times 10^{-3}$  (D)  $-1.2 \times 10^{-2}$
16. For a dilute solution containing 2.5 g of a non-volatile non-electrolyte solute in 100 g of water, the elevation in boiling point at 1 atm pressure is  $2^{\circ}\text{C}$ . Assuming concentration of solute is much lower than the concentration of solvent, the vapour pressure (mm of Hg) of the solution is (take  $K_b = 0.76 \text{ K kg mol}^{-1}$ ) [JEE 2012]  
 (A) 724 (B) 740 (C) 736 (D) 718
17. Benzene and naphthalene form an ideal solution at room temperature. For this process, the true statement(s) is(are) [J-Adv. 2013]  
 (A)  $\Delta G$  is positive (B)  $\Delta S_{\text{system}}$  is positive (C)  $\Delta S_{\text{surroundings}} = 0$  (D)  $\Delta H = 0$
18. If the freezing point of a 0.01 molal aqueous solution of a cobalt (III) chloride-ammonia complex (which behaves as a strong electrolyte) is  $-0.0558^{\circ}\text{C}$ , the number of chloride (s) in the coordination sphere of the complex is- [ $K_f$  of water =  $1.86 \text{ K kg mol}^{-1}$ ] [JEE-Adv. 2015]
19. Mixture(s) showing positive deviation from Raoult's law at  $35^{\circ}\text{C}$  is (are) [JEE-Adv. 2016]  
 (A) carbon tetrachloride + methanol  
 (B) carbon disulphide + acetone  
 (C) benzene + toluene  
 (D) phenol + aniline
20. For a solution formed by mixing liquids L and M, the vapour pressure of L plotted against the mole fraction of M in solution is shown in the following figure, Here  $x_L$  and  $x_M$  represent mole fractions of L and M, respectively, in the solution. the correct statement(s) applicable to this system is(are)



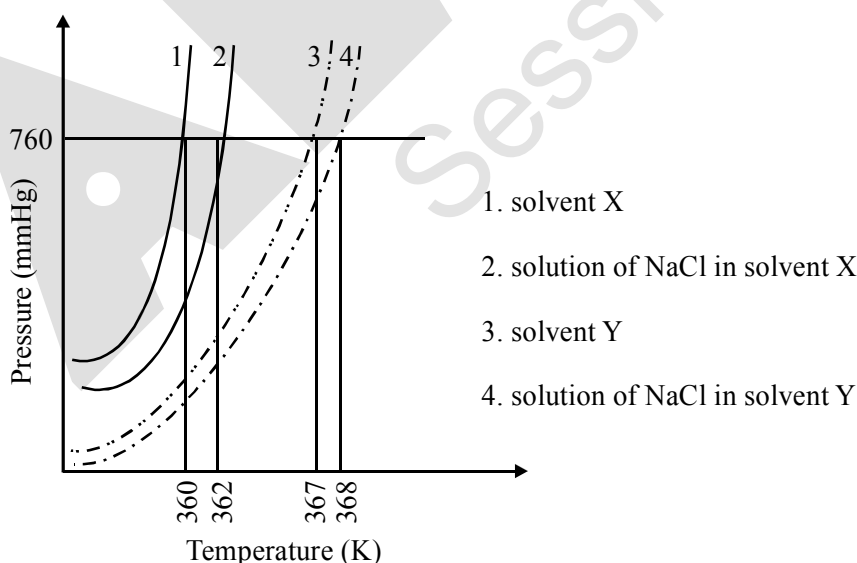
- (A) Attractive intramolecular interactions between L-L in pure liquid L and M-M in pure liquid M are stronger than those between L-M when mixed in solution [JEE-Adv. 2017]  
 (B) The point Z represents vapour pressure of pure liquid M and Raoult's law is obeyed when  $x_L \rightarrow 0$   
 (C) The point Z represents vapour pressure of pure liquid L and Raoult's law is obeyed when  $x_L \rightarrow 1$   
 (D) The point Z represents vapour pressure of pure liquid M and Raoult's law is obeyed from  $x_L = 0$  to  $x_L = 1$

21. Pure water freezes at 273 K and 1 bar. The addition of 34.5 g of ethanol to 500 g of water changes the freezing point of the solution. Use the freezing point depression constant of water as  $2 \text{ K kg mol}^{-1}$ . The figures shown below represents plots of vapour pressure (V.P.) versus temperature (T). [Molecular weight of ethanol is  $46 \text{ g mol}^{-1}$ ]

Among the following, the option representing change in the freezing point is - [JEE-Adv. 2017]



22. Liquids A and B form ideal solution over the entire range of composition. At temperature T, equimolar binary solution of liquids A and B has vapour pressure 45 Torr. At the same temperature, a new solution of A and B having mole fractions  $x_A$  and  $x_B$ , respectively, has vapour pressure of 22.5 Torr. The value of  $x_A/x_B$  in the new solution is \_\_\_\_\_. [JEE-Adv. 2018]
- (Given that the vapour pressure of pure liquid A is 20 Torr at temperature T)
23. The plot given below shows P–T curves (where P is the pressure and T is the temperature) for two solvents X and Y and isomolal solutions of NaCl in these solvents. NaCl completely dissociates in both the solvents.



On addition of equal number of moles a non-volatile solute S in equal amount (in kg) of these solvents, the elevation of boiling point of solvent X is three times that of solvent Y. Solute S is known to undergo dimerization in these solvents. If the degree of dimerization is 0.7 in solvent Y, the degree of dimerization in solvent X is \_\_\_\_\_. [JEE-Adv. 2018]

# ANSWER-KEY

## EXERCISE # S-I

- |                                                                  |                                                                         |
|------------------------------------------------------------------|-------------------------------------------------------------------------|
| 1. Ans. 0.25                                                     | 2. Ans. 64.0 mm Hg                                                      |
| 3. Ans. $P_A^0 = 100 \text{ cmHg}$ , $P_B^0 = 60 \text{ cmHg}$ . | 4. Ans. 0.25                                                            |
| 5. Ans. 0.5 bar                                                  | 6. Ans. $P_X^0 = 55 \text{ cmHg}$ , $P_Y^0 = 80 \text{ cmHg}$           |
| 7. Ans. $P_R^0 = 0.8 \text{ bar}$ , $P_S^0 = 0.4 \text{ bar}$    | 8. Ans. 0.25                                                            |
| 9. Ans. 0.04                                                     | 10. Ans. 0.32 m                                                         |
| 11. Ans. 65.25                                                   | 12. Ans. 17.38 mm Hg                                                    |
| 13. Ans. 120 g/mol                                               | 14. Ans. $K_b = 0.516 \text{ kg mol K}^{-1}$ , $T_b = 373.20 \text{ K}$ |
| 15. Ans. 5.1 K-k/mol                                             | 16. Ans. 2048 g/mol                                                     |
| 17. Ans. (6.972)                                                 | 18. Ans. 40 g/mol                                                       |
| 19. Ans. 49.26 atm                                               | 20. Ans. 3.69 atm                                                       |
| 21. Ans. 1.96                                                    | 22. Ans. 3 ions                                                         |
| 23. Ans. 78 %                                                    | 24. Ans. $7.482 \times 10^5 \text{ Nm}^{-2}$                            |
| 25. Ans. 0.95; 1.95                                              | 26. Ans. 0.04                                                           |
| 27. Ans. (3)                                                     |                                                                         |

## EXERCISE # S-II

- |                                             |                                                          |
|---------------------------------------------|----------------------------------------------------------|
| 1. Ans. 92 mol% toluene; 96.8 mol % toluene | 2. Ans. 0.741 m, 0.0136                                  |
| 3. Ans. 38.71 g                             | 4. Ans. $4.8 \times 10^4 \text{ g/mol}$                  |
| 5. Ans. (777)                               | 6. Ans. (68.4)                                           |
| 7. Ans. $C_{40}H_{80}O_{40}$                | 8. Ans. $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ |
| 9. Ans. $a = 0.50$                          | 10. Ans. 0.73                                            |
| 11. Ans. (9)                                | 12. Ans. (60%)                                           |
| 13. Ans. (3.2)                              | 14. Ans. (100°C)                                         |
| 15. Ans. $C_6H_6$                           |                                                          |

## EXERCISE # O-I

- |              |              |              |              |
|--------------|--------------|--------------|--------------|
| 1. Ans. (B)  | 2. Ans. (C)  | 3. Ans. (C)  | 4. Ans. (D)  |
| 5. Ans. (A)  | 6. Ans. (C)  | 7. Ans. (C)  | 8. Ans. (C)  |
| 9. Ans. (D)  | 10. Ans. (C) | 11. Ans. (C) | 12. Ans. (A) |
| 13. Ans. (A) | 14. Ans. (B) | 15. Ans. (B) | 16. Ans. (B) |
| 17. Ans. (C) | 18. Ans. (D) | 19. Ans. (B) | 20. Ans. (A) |
| 21. Ans. (C) | 22. Ans. (B) | 23. Ans. (D) | 24. Ans. (B) |
| 25. Ans. (B) | 26. Ans. (D) | 27. Ans. (B) | 28. Ans. (D) |
| 29. Ans. (B) | 30. Ans. (B) | 31. Ans. (D) | 32. Ans. (B) |
| 33. Ans. (B) | 34. Ans. (B) | 35. Ans. (A) | 36. Ans. (D) |

## EXERCISE # O-II

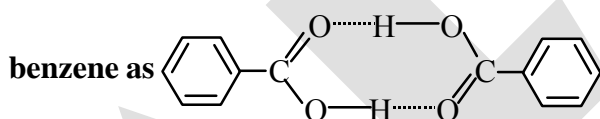
- |                                                                                                                  |                 |                    |                |
|------------------------------------------------------------------------------------------------------------------|-----------------|--------------------|----------------|
| 1. Ans. (B)                                                                                                      | 2. Ans. (D)     | 3. Ans. (A)        | 4. Ans. (A)    |
| 5. Ans. (B)                                                                                                      | 6. Ans. (D)     | 7. Ans. (C)        | 8. Ans. (C)    |
| 9. Ans. (C)                                                                                                      | 10. Ans. (C, D) | 11. Ans. (A,B,C,D) | 12. Ans. (C,D) |
| 13. Ans. (C)                                                                                                     | 14. Ans. (C)    | 15. Ans. (B)       | 16. Ans. (C)   |
| 17. Ans. (D)                                                                                                     | 18. Ans. (C)    | 19. Ans. (A)       | 20. Ans. (C)   |
| 21. Ans. (A) $\rightarrow$ P ; (B) $\rightarrow$ Q, R, S ; (C) $\rightarrow$ T ; (D) $\rightarrow$ P, Q, R, S, T |                 |                    |                |

## EXERCISE # (J-MAIN)

- |              |              |              |              |
|--------------|--------------|--------------|--------------|
| 1. Ans. (3)  | 2. Ans. (3)  | 3. Ans. (3)  | 4. Ans. (1)  |
| 5. Ans. (1)  | 6. Ans. (3)  | 7. Ans. (3)  | 8. Ans. (1)  |
| 9. Ans. (4)  | 10. Ans. (1) | 11. Ans. (4) | 12. Ans. (2) |
| 13. Ans. (3) | 14. Ans. (1) | 15. Ans. (1) | 16. Ans. (4) |
| 17. Ans. (1) | 18. Ans. (3) | 19. Ans. (4) | 20. Ans. (4) |
| 21. Ans. (1) | 22. Ans. (2) | 23. Ans. (3) | 24. Ans. (1) |
| 25. Ans. (4) |              |              |              |

## EXERCISE # (J-ADVANCED)

- |                                                                                                  |                                               |
|--------------------------------------------------------------------------------------------------|-----------------------------------------------|
| 1. Ans. 0.23 K                                                                                   | 2. Ans. $(1.0 \times 10^{-4})\text{min}^{-1}$ |
| 3. Ans. $K_p(x) = 0.68$ , $K_p(y) = 0.53$ , $K_p(z) = 0.98$                                      | 4. Ans. (A)                                   |
| 5. Ans. (a)122, (b) It means that benzoic acid remains as it is in acetone while it dimerises in |                                               |



- |                                    |                 |                |                  |
|------------------------------------|-----------------|----------------|------------------|
| 6. Ans. (C)                        | 7. Ans. (C)     |                |                  |
| 8. Ans. 35% (degree of asso = 70%) | 9. Ans. (A)     |                |                  |
| 10. Ans. (D)                       | 11. Ans. (B)    | 12. Ans. (B)   | 13. Ans. (A)     |
| 14. Ans. (A)                       | 15. Ans. (A)    | 16. Ans. (A)   | 17. Ans. (B,C,D) |
| 18. Ans. (1)                       | 19. Ans. (A,B)  | 20. Ans. (A,C) | 21. Ans. (D)     |
| 22. Ans. (19)                      | 23. Ans. (0.05) |                |                  |

## CHEMICAL KINETICS

### 1. INTRODUCTION

Chemical kinetics deals with the rates of chemical processes. Any chemical process may be broken down into a sequence of one or more single-step processes known either as elementary processes, elementary reactions, or elementary steps. Elementary reactions usually involve either a single reactive collision between two molecules, which we refer to as a bimolecular step, or dissociation/isomerisation of a single reactant molecule, which we refer to as a unimolecular step. Very rarely, under conditions of extremely high pressure, a termolecular step may occur, which involves simultaneous collision of three reactant molecules. An important point to recognise is that, many reactions that are written as a single reaction equation, in actual fact, consist of a series of elementary steps. This will become extremely important as we learn more about the theory of chemical reaction rates.

As a general rule, elementary processes involve a transition between two atomic or molecular states separated by a potential barrier. The potential barrier constitutes the activation energy of the process, and determines the rate at which it occurs. When the barrier is low, the thermal energy of the reactants will generally be high enough to surmount the barrier and move over to products, and the reaction will be fast. However, when the barrier is high, only a few reactants will have sufficient energy, and the reaction will be much slower. The presence of a potential barrier to reaction is also the source of the temperature dependence of reaction rates.

The huge variety of chemical species, types of reaction, and the accompanying potential energy surfaces involved means that the time scale over which chemical reactions occur covers many orders of magnitude, from very slow reactions, such as iron rusting, to extremely fast reactions, such as the electron transfer processes involved in many biological systems or the combustion reactions occurring in flames.

A study into the kinetics of a chemical reaction is usually carried out with one or both of two main goals in mind :

- (i) Analysis of the sequence of elementary steps giving rise to the overall reaction. i.e. the reaction mechanism.
- (ii) Determination of the absolute rate of the reaction and/or its individual elementary steps.

### 2. CLASSIFICATION OF REACTION

- (i) There are certain reactions which are too slow. **Ex.** Rusting of Iron, weathering of rocks.
- (ii) Instantaneous reactions i.e. too fast. **Ex.** Detonation of explosives, acid-base neutralization, precipitation of AgCl by NaCl and AgNO<sub>3</sub>.
- (iii) Neither too fast nor too slow. **Ex.** Combination of H<sub>2</sub> and Cl<sub>2</sub> in presence of light, hydrolysis of ethyl acetate catalysed by acid, decomposition of Azomethane.



### 3. Types of Rates of chemical reaction :

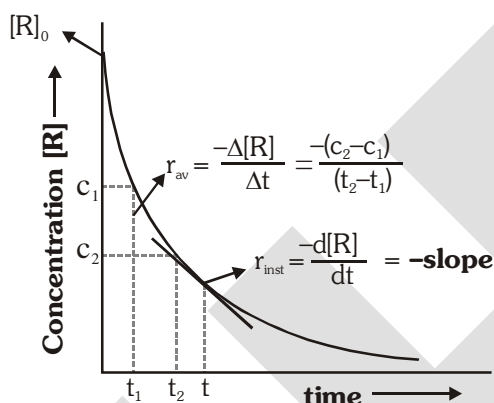
For a reaction  $R \longrightarrow P$ ,

- Average rate** =  $\frac{\text{Total change in concentration}}{\text{Total time taken}} = \frac{|\Delta c|}{\Delta t} = -\frac{\Delta[\text{Reactant}]}{\Delta t} = \frac{\Delta[\text{Product}]}{\Delta t}$
- Instantaneous rate** : Rate of reaction at a particular instant.

$$R_{\text{instantaneous}} = \lim_{\Delta t \rightarrow 0} \left[ \frac{|\Delta c|}{\Delta t} \right] = \left| \frac{dc}{dt} \right| = -\frac{d[R]}{dt} = \frac{d[P]}{dt}$$

Instantaneous rate can be determined from slope of a tangent at time  $t$  on curve drawn for concentration versus time.

#### 3.1 Initial Rate : Instantaneous rate at ' $t = 0$ ' is called initial rate [Slope of tangent at $t = 0$ ].



#### ❖ Reaction rates and stoichiometry :

We have seen that for stoichiometrically simple reactions of the type  $A \rightarrow B$ , the rate can be either expressed in terms of the decrease in reactant concentration with time,  $-\Delta[A]/\Delta t$  or the increase in product concentration with time,  $\Delta[B]/\Delta t$ . For more complex reactions, we must be careful in writing the rate expressions. Consider for example, the reaction,



Two moles of A disappear for each mole of B that forms – that is, the rate of disappearance of A is twice as fast as the rate of appearance of B. We write the overall rate of reaction as either

$$\text{Rate} = -\frac{1}{2} \frac{\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t}$$

In general, for the reaction,  $aA + bB \longrightarrow cC + dD$

the rate is given by

$$\text{Rate} = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t}$$

**Ex. :** For the reaction in terms :  $\text{N}_2 + 3\text{H}_2 \longrightarrow 2\text{NH}_3$

Rate of reaction in terms of  $\text{N}_2 = -\frac{d[\text{N}_2]}{dt}$  = rate of disappearance of  $\text{N}_2$

Rate of reaction in terms of  $\text{H}_2 = -\frac{d[\text{H}_2]}{dt}$  = rate of disappearance of  $\text{H}_2$

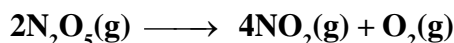
Rate of reaction in terms of  $\text{NH}_3 = \frac{d[\text{NH}_3]}{dt}$  = rate of appearance of  $\text{NH}_3$

These rates are not all equal. Therefore, by convention, the rate of a reaction is defined as

• **Rate of reaction**  $= -\frac{d[\text{N}_2]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt}$

**Note:** The value of rate of reaction is dependent on the stoichiometric coefficients used in the reaction while the rate of increase or decrease in amount of any species will be fixed value under given conditions.

**Ex.1** The following reaction was studied in a closed vessel



It was found that the concentration of  $\text{NO}_2$  increases by  $2.0 \times 10^{-2} \text{ mol L}^{-1}$  in five seconds. Calculate.

(i) The rate of reaction

(ii) The rate of decrease of concentration of  $\text{N}_2\text{O}_5$

**Sol.** (i) Rate of reaction  $= \frac{1}{4} \frac{d[\text{NO}_2]}{dt}$

But  $\frac{d[\text{NO}_2]}{dt} = \frac{2.0 \times 10^{-2} \text{ mol L}^{-1}}{5\text{s}} = 4 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$

Rate of reaction  $= \frac{1}{4} \times 4 \times 10^{-3} = 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$

(ii) Rate of decrease of conc. of  $\text{N}_2\text{O}_5$

$$\begin{aligned} &= -\frac{d[\text{N}_2\text{O}_5]}{dt} = -\frac{1}{2} \times \text{Rate of formation of } \text{NO}_2 = +\frac{1}{2} \frac{d[\text{NO}_2]}{dt} \\ &= +\frac{1}{2} \times 4 \times 10^{-3} = 2 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1} \end{aligned}$$

### 3.3 FACTORS AFFECTING RATE OF CHEMICAL REACTION

(i) Concentration

(iii) Nature of reactants and products

(v) pH of the solution

(vii) Radiations / light

(ix) Electrical and magnetic field.

(ii) Temperature

(iv) Catalyst

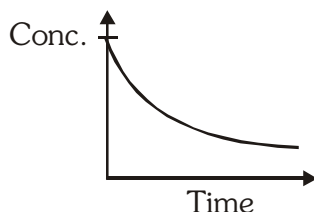
(vi) Dielectric constant of the medium.

(viii) Pressure

The first four factors generally affect rate of almost all reactions while other factors are specific to some reactions only.

**(i) Effect of concentration :**

For most of the reactions, rate depends on concentration of reactants. So rate of reaction decreases with passage of time, since concentration of reactants decreases.

**(ii) Effect of temperature :** Generally rate of reaction increases on increasing temperature.**(iii) Effect of nature of reactants and products :**

- (a) Physical state of reactants :** Gaseous state > Liquid state > Solid state  
(Decreasing order of rate of reaction)

Because collisions in gaseous systems are more effective than condensed systems (solid & liquid).

- (b) Physical size of reactants :** In heterogeneous reactions, as we decrease the particle size, rate of reaction increases since surface area increases.

**(c) Chemical nature of reactants :**

- If more bonds are to be broken, the rate of reaction will be slow.
- Similarly if bond strength in reactants is more, rate of reaction will be slow.

**(iv) Effect of Catalyst :**

- Presence of positive catalyst lowers down the activation energy hence increases the rate of reaction.
- Presence of negative catalyst increases activation energy hence decreases the rate of reaction.

**(v) Effect of pH of solution : Ex.**  $[\text{Fe}(\text{CN})_6]^{4-} \xrightarrow{(\text{Ti}^{3+})} [\text{Fe}(\text{CN})_6]^{3-}$ 

This reaction takes place with appreciable rate in acidic medium, but does not take place in basic medium.

**(vi) Effect of dielectric constant of the medium :** More is the dielectric constant of the medium greater will be the rate of ionic reactions.**(vii) Effect of radiations / light :** Radiations are useful for photochemical reactions.**(viii) Effect of pressure :** Pressure is important factor for gaseous reactions.**(ix) Effect of electrical & magnetic field :** Electric and magnetic fields are rate determining factors if a reaction involves polar species.**4. RATE LAW (DEPENDENCE OF RATE ON CONCENTRATION OF REACTANTS) :**

The representation of rate of reaction in terms of the concentration of the reactants is called the rate law. It can only be established by experiments.

Generally rate law expressions are not simple and these may differ for the same reaction on conditions under which the reaction is being carried out. But for large number of reactions starting with pure reactants we can obtain simple rate laws. For these reactions :

$$\text{Rate} \propto (\text{conc.})^{\text{order}}$$

$$\text{Rate} = K (\text{conc.})^{\text{order}} \quad \text{This is the differential rate equation or rate expression.}$$

Where  $K$  = Rate constant = specific reaction rate = rate of reaction when concentration is unity

$$\text{unit of } K = (\text{conc})^{1-\text{order}} \text{ time}^{-1}$$

**Note:** Value of  $K$  is a constant for a given reaction, depending only on temperature and catalyst use.

#### 4.1 Order of reaction :

Let there be a reaction,  $m_1A + m_2B \longrightarrow \text{products}$ .

Now, if on the basis of experiment, we find that

$$R \propto [A]^p [B]^q$$

where  $p$  may or may not be equal to  $m_1$  and similarly  $q$  may or may not be equal to  $m_2$ .

$p$  is order of reaction with respect to reactant  $A$  and  $q$  is order of reaction with respect to reactant  $B$  and  $(p + q)$  is **overall order of the reaction**.

**Note:** Order of a reaction can be 'zero', any whole number, fractional number or even be negative with respect to a particular reactant.

#### ❖ Examples showing different values of order of reactions :

| Reaction                                                                  | Rate law                         | Order           |
|---------------------------------------------------------------------------|----------------------------------|-----------------|
| (i) $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$                            | $R = K [N_2O_5]^1$               | 1               |
| (ii) $5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \rightarrow 3Br_2(l) + 3H_2O(l)$ | $R = K [Br^-][BrO_3^-][H^+]^2$   | $1 + 1 + 2 = 4$ |
| (iii) $H_2(\text{Para}) \rightarrow H_2(\text{ortho})$                    | $R = K [H_2(\text{Para})]^{3/2}$ | $3/2$           |
| (iv) $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$                        | $R = K [NO_2]^2 [CO]^0$          | $2 + 0 = 2$     |
| (v) $2O_3(g) \rightarrow 3O_2(g)$                                         | $R = K [O_3]^2 [O_2]^{-1}$       | $2 - 1 = 1$     |
| (vi) $H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$                                 | $R = K [H_2]^0 [Cl_2]^0$         | $0 + 0 = 0$     |

The reaction (ii) does not take place in one single step. It is almost impossible for all the 12 molecules of the reactants to be in a state of encounter simultaneously. Such a reaction is called **Complex reaction** and takes place in a sequence of a number of **Elementary reactions**. For an elementary reaction, the sum of stoichiometric coefficients of reactants = order of the reaction. But for complex reactions, order is to be experimentally calculated.

#### 4.2 Molecularity of reaction :

The number of molecules that react in an elementary step is the molecularity of the elementary reaction. Molecularity is defined only for the elementary reactions and not for complex reactions. No elementary reactions involving more than three molecules are known, because of very low probability of simultaneous collision of more than three molecules.

The rate law for the elementary reaction



For an elementary reaction, the orders in the rate law equal the coefficients of the reactants. It must be noted that the order is defined for complex as well as elementary reactions and is always experimentally calculated from the mechanism of the reaction, usually by the slowest step of the mechanism known as rate determining step (RDS) of the reaction.

| Comparison between molecularity and order of reaction |                                                                                                                                                                                      |                   |                                                                                                                                                                                                                    |
|-------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Molecularity of Reaction                              |                                                                                                                                                                                      | Order of Reaction |                                                                                                                                                                                                                    |
| 1                                                     | It is defined as the no. of molecules of reactant taking part in a chemical reaction.<br>$\text{NH}_4\text{NO}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$ ,<br>molecularity = 1 | 1                 | It is defined as the sum of the power of concentration terms that appear in rate law.<br>$\text{NH}_4\text{NO}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$ .<br>Rate = $k[\text{NH}_4\text{NO}_2]$ , order = 1 |
| 2                                                     | It is always a whole number.<br>It can neither be zero nor fractional.                                                                                                               | 2                 | It may be zero, fractional or integer.                                                                                                                                                                             |
| 3                                                     | It is derived from RDS in the mechanism of reaction                                                                                                                                  | 3                 | It is derived from rate expression.                                                                                                                                                                                |
| 4                                                     | It is theoretical value.                                                                                                                                                             | 4                 | It is experimental value.                                                                                                                                                                                          |
| 5                                                     | Reactions with molecularity > 3 are rare.                                                                                                                                            | 5                 | Reactions with order of reaction > 4 are also rare.                                                                                                                                                                |
| 6                                                     | Molecularity is independent of pressure and temperature.                                                                                                                             | 6                 | Order of reaction may depend upon pressure and temperature.                                                                                                                                                        |

## 5. INTEGRATED RATE LAW :

For a single reactant reaction where the chemical equation has the form



and the rate law is assumed to be of the form

$$\text{Rate} = -d[A]/dt = k[A]^m$$

Where  $m$  is the order of the reaction with respect to substance  $A$ . Three important cases can be treated :  $m = 0$ ,  $m = 1$ , and  $m = 2$ . These are called *zeroth order*, *first order*, and *second order*, respectively.

### 5.1 Zero - order reaction :

For a reaction where the chemical equation has the form



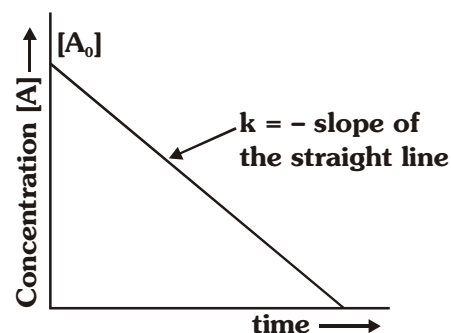
and the rate law is assumed to be of the form

$$\text{Rate} = -d[A]/dt = k[A]^0$$

$$-\int_{C_0}^{C_t} d[A] = k \int_0^t dt$$

$$k = \frac{C_0 - C_t}{t'}$$

$$\text{or } kt = C_0 - C_t \quad \text{or} \quad C_t = C_0 - kt$$



- Unit of K is same as that of Rate = mol lit<sup>-1</sup> sec<sup>-1</sup>.
- Time for completion =  $\frac{C_0}{k}$
- $t_{1/2}$  (half life period)

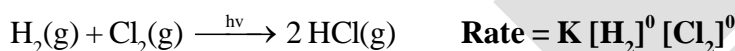
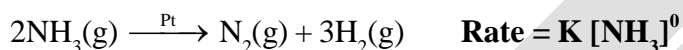
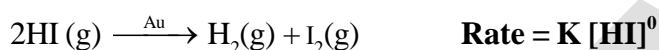
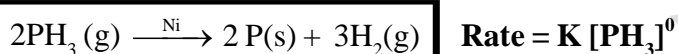
$$\text{At } t_{1/2}, C_t = \frac{C_0}{2},$$

$$\text{So } kt_{1/2} = \frac{C_0}{2} \Rightarrow t_{1/2} = \frac{C_0}{2k}$$

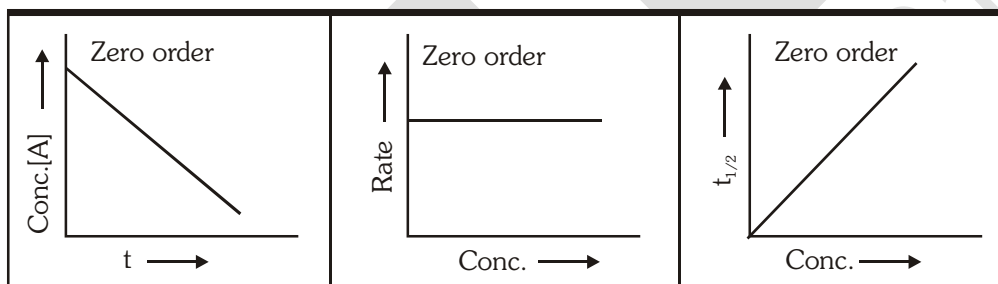
$$\therefore t_{1/2} \propto C_0$$

❖ **Examples of Zero order reactions :**

Generally decomposition of gases on metal surfaces at high concentrations follow zero order kinetics as rate depends on surface area of catalyst.



❖ **Graphs :**



**Ex.2** For the zero order reaction :  $\text{A} \rightarrow \text{P}$ ,  $K = 10^{-2} \text{ (mol/litre) sec}^{-1}$  If initial concentration of A is 0.3M, then find concentration of A left at 10 sec.

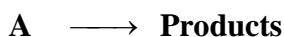
- (A) 0 M                      (B) 0.2 M                      (C) 0.1 M                      (D) 0.15 M

**Sol. (B)**

$$[\text{A}]_t = [\text{A}]_0 - Kt = 0.3 - 10^{-2} \times 10 = 0.2 \text{ M}$$

**5.2 First order reaction :**

Consider a first order reaction with single reactant.



$$t = 0 \quad a \quad 0$$

$$t = t \quad a-x$$

$$\text{Rate} = -\frac{d[\text{A}]}{dt} = k [\text{A}]^1$$

$$\therefore \frac{dx}{dt} = k(a-x)^1 \quad \text{or} \quad \frac{dx}{a-x} = kdt.$$

- On solving  $k = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{t} \log \frac{C_0}{C_t}$

$$K = \frac{2.303}{t} \log \frac{C_0}{C_t} \quad \text{Wilhemmy formula : } C_t = C_0 e^{-kt} \quad \text{Interval formula : } k = \frac{2.303}{(t_2 - t_1)} \log \frac{C_1}{C_2}$$

- Unit of  $k = \text{sec}^{-1}, \text{min}^{-1}, \text{etc.}$

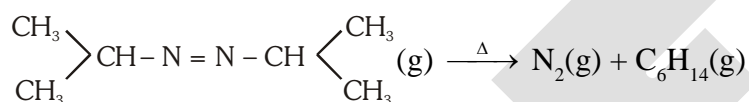
- Half-life time ( $t_{1/2}$ ) :**

$$k = \frac{2.303}{t_{1/2}} \log \frac{2C_0}{C_0} \Rightarrow t_{1/2} = \frac{2.303 \log 2}{k} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

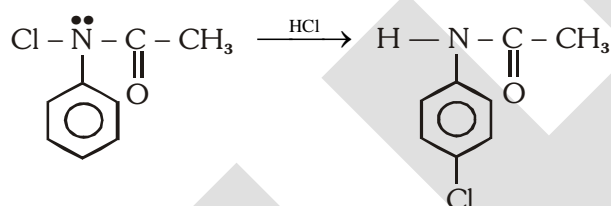
$\therefore$  Half-life period for a first order reaction is a constant quantity at given temperature.

- Examples of first order reactions :**

- (i) Decomposition of azoisopropane



- (ii) Conversion of N-chloro acetanilide into p-chloroacetanilide



- (iii)  $\text{H}_2\text{O}_2(\text{aq.}) \longrightarrow \text{H}_2\text{O}(\text{l}) + \frac{1}{2} \text{O}_2(\text{g})$

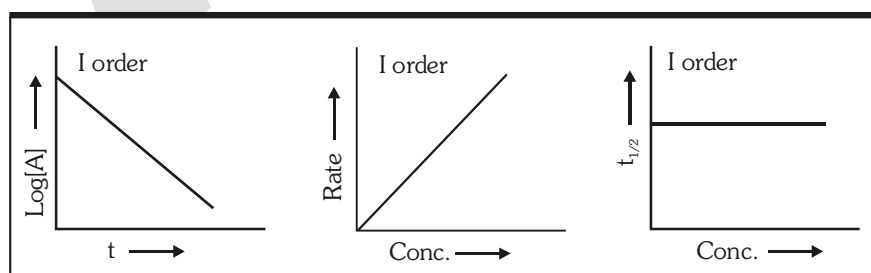
- (iv)  $\text{NH}_4\text{NO}_2 \longrightarrow 2\text{H}_2\text{O}(\text{g}) + \text{N}_2(\text{g})$

- (v) Radioactive decay

All radioactive decays always follow first order kinetics.



- Graphs :**



**Ex.3** Calculate  $\frac{t_{0.75}}{t_{0.50}}$  for a first order reaction :

**Sol.**  $k = \frac{2.303}{t_{3/4}} \log \frac{C_0}{\frac{1}{4}C_0} = \frac{2.303}{t_{1/2}} \log \frac{C_0}{\frac{C_0}{2}} \Rightarrow \frac{t_{3/4}}{t_{1/2}} = \frac{\log 4}{\log 2} = \frac{2 \log 2}{\log 2} = 2$

**Ex.4** 90% of a first order reaction was completed in 10 hours. When will 99.9% of the reaction complete ?

**Sol.**  $K = \frac{2.303}{t} \log \frac{a}{a-x}$

$a = 100, x = 90, t = 10$

So  $K = \frac{2.303}{10} \log \frac{100}{10}$

$K = 2.303 \times 10^{-1} \text{ hour}^{-1}$

Now for 99.9% completion -

$a = 100$  and  $x = 99.9$

$t = \frac{2.303}{K} \log \frac{100}{0.1} = \frac{2.303}{2.303 \times 10^{-1}} \times 3 = 30 \text{ hours}$

**Ex.5** A first order reaction is 90% complete after 40 min. Calculate the half life of reaction.

**Sol.**  $a = 100, x = 90$

$K_1 = \frac{2.303}{t} \log \frac{a}{a-x}$

$= \frac{2.303}{40} \log \frac{100}{10}$

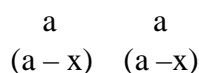
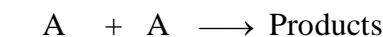
$= \frac{2.303}{40} = 5.757 \times 10^{-2} \text{ min}^{-1}$

$t_{1/2} = \frac{0.693}{K_1} = \frac{0.693}{5.757 \times 10^{-2}} = 12.03 \text{ min.}$

### 5.3.1 Second order reaction :

•

#### Case : 1



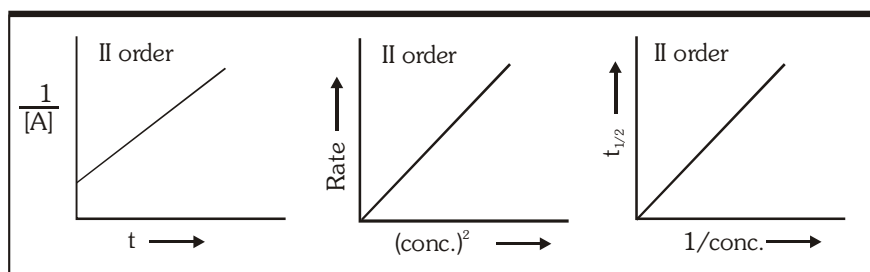
$\therefore \frac{dx}{dt} = k(a-x)^2$

$\Rightarrow \frac{1}{(a-x)} - \frac{1}{a} = kt \quad \text{or} \quad \frac{1}{C_t} - \frac{1}{C_0} = kt$

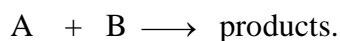


- Unit of  $k = \text{Lmol}^{-1} \text{sec}^{-1}$
- Half life,  $t_{1/2} = \frac{1}{k.C_0}$

• **Graphs :**



**5.3.2 Case : 2**



Rate law

$$\frac{dx}{dt} = k(a - x)(b - x)$$

$$\int_0^x \frac{dx}{(a-x)(b-x)} = \int_0^t k dt$$

$$k = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)} \quad (\text{no need to remember})$$

where  $a \neq b$

**Ex.6** For a second order reaction in which both the reactants have equal initial concentration, the time taken for 60% completion of reaction is 3000 second. What will be the time taken for 20% of the reaction?

**Sol.**  $k_2 = \frac{1}{t} \frac{x}{a(a-x)}$

Let  $a = 1$ ,

$$k_2 = \frac{1}{t} \frac{x}{1(1-x)}$$

$$= \frac{1}{3000} \left( \frac{0.6}{1-0.6} \right)$$

$$= \frac{1}{3000} \times \frac{0.6}{0.4} = \frac{1}{2000}$$

So time for the 20% completion :

$$t = \frac{1}{k_2} \frac{x}{a(a-x)}$$

$$= 2000 \times \frac{0.20}{0.80} = 500 \text{ sec.}$$

### 5.4 Pseudo order reaction :

For,  $A + B \longrightarrow \text{Products}$

$t=0$      $a$                        $b$

$t=t$      $a-x$                        $b-x$

$$\text{Rate} = K [A]^n [B]^m$$

If  $[B] = \text{constant} \Rightarrow [b-x] \approx \text{constant}$

$$\text{Rate} = K' [A]^n$$

$$\text{when } K' = K[B]^m$$

- **Case 1 :**

If concentration of B is much greater than A, then  $[B] = \text{Constant} \Rightarrow [b-x] \approx \text{Constant}$ .

- **Case 2 :**

If B is a catalyst, then  $[B] = \text{Constant} \Rightarrow [b-x] \approx \text{Constant}$ .

- **Case 3 :**

If B is a solvent, then  $[B] = \text{Constant} \Rightarrow [b-x] \approx \text{Constant}$ .

### 5.4.1 PSEUDO FIRST ORDER REACTIONS :

A second order (or of higher order) reactions can be converted into a first order reaction if the other reactant is taken in large excess. Such first order reactions are known as **pseudo first order reactions**.

$\therefore$  For  $A + B \longrightarrow \text{Products}$     **[Rate] =  $K [A]^1 [B]^1$**

$$K = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)} \quad (\text{from 5.3.2})$$

Now if 'B' is taken in large excess  $b \gg a$ .

$$\therefore K = \frac{2.303}{-bt} \log \frac{(a-x)}{a} \Rightarrow K = \frac{2.303}{bt} \log \frac{a}{a-x}$$

$$\Rightarrow K.b = \frac{2.303}{t} \log \frac{a}{a-x} \Rightarrow K' = \frac{2.303}{t} \log \frac{a}{a-x}$$

$K'$  is pseudo first order rate constant.

$K'$  will have units of first order.

$K$  will have units of second order.

❖ **Table :** Characteristics of Zero, First, Second and  $n^{\text{th}}$  order reactions of the type  $A \longrightarrow \text{Products}$

|                       | Zero order                                            | First order                                              | Second order                                          | $n^{\text{th}}$ order                                     |
|-----------------------|-------------------------------------------------------|----------------------------------------------------------|-------------------------------------------------------|-----------------------------------------------------------|
| Differential Rate law | $-\frac{d[A]}{dt} = k[A]^0$                           | $-\frac{d[A]}{dt} = k[A]$                                | $-\frac{d[A]}{dt} = k[A]^2$                           | $-\frac{d[A]}{dt} = k[A]^n$                               |
| Integrated Rate law   | $[A]_t = [A]_0 - kt$                                  | $\ln[A]_t = -kt + \ln[A]_0$                              | $\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$              | $\frac{1}{[A]_t^{n-1}} - \frac{1}{[A]_0^{n-1}} = (n-1)kt$ |
| Linear graph          | $[A]_t$ v/s $t$                                       | $\ln[A]$ v/s $t$                                         | $\frac{1}{[A]}$ v/s $t$                               | $\frac{1}{[A]^{n-1}}$ v/s $t$                             |
| Half-life             | $t_{1/2} = \frac{[A]_0}{2k}$<br>(depends on $[A]_0$ ) | $t_{1/2} = \frac{0.693}{k}$<br>(independent of $[A]_0$ ) | $t_{1/2} = \frac{1}{k[A]_0}$<br>(depends on $[A]_0$ ) | $t_{1/2} \propto \frac{1}{[A]_0^{n-1}}$                   |

## 6 Methods to determine order of a reaction :

### 6.1 Initial rate method :

By comparison of different initial rates of a reaction by varying the concentration of one of the reactants while others are kept constant.

$$r = k [A]^a [B]^b [C]^c \quad \text{if } [B] = \text{constant and } [C] = \text{constant}$$

then for two different initial concentrations of A we have

$$r_{01} = k [A_0]_1^a \quad r_{02} = k [A_0]_2^a \quad \Rightarrow \quad \frac{r_{01}}{r_{02}} = \left( \frac{[A_0]_1}{[A_0]_2} \right)^a$$

or in log form we have 
$$a = \frac{\log(r_{01}/r_{02})}{\log([A_0]_1/[A_0]_2)}$$

### 6.2 Integrated rate law method :

It is method of hit and trial. By checking if the kinetic data (experimental data) best fits into a particular integrated rate law, we determine the order. It can also be done graphically.

**Ex.7** The rate of decomposition of  $N_2O_5$  in  $CCl_4$  solution has been studied at 318 K and the following results have been obtained :

|       |      |      |      |      |      |
|-------|------|------|------|------|------|
| t/min | 0    | 135  | 342  | 683  | 1693 |
| c/M   | 2.08 | 1.91 | 1.67 | 1.35 | 0.57 |

Find the order of the reaction and calculate its rate constant. What is the half-life period?

**Sol.** It can be shown that these data will not satisfy the integrated rate law of zero order. We now try integrated first order equation i.e.,  $k = \frac{\ln(c_0/c)}{t}$ .

| t / min | c / M | $k = \frac{\ln(c_0/c)}{t} \text{ min}^{-1}$ |
|---------|-------|---------------------------------------------|
| 0       | 2.08  | $6.32 \times 10^{-4}$                       |
| 135     | 1.91  | $6.30 \times 10^{-4}$                       |
| 339     | 1.68  | $6.32 \times 10^{-4}$                       |
| 683     | 1.35  | $6.32 \times 10^{-4}$                       |
| 1680    | 0.72  | $6.31 \times 10^{-4}$                       |

It can be seen that the value of  $k$  is almost constant for all the experimental results and hence it is first order reaction with  $k = 6.31 \times 10^{-4} \text{ min}^{-1}$ .

$$t_{1/2} = \frac{0.693}{6.31 \times 10^{-4} \text{ min}^{-1}} = 1.094 \times 10^3 \text{ min}^{-1}$$

### 6.3 Method of half lives :

The half lives of each order is unique so by comparing half lives we can determine order for  $n^{\text{th}}$

order reaction  $t_{1/2} \propto \frac{1}{[A_0]^{n-1}}$  (Remember)

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \frac{[A_0]_2^{n-1}}{[A_0]_1^{n-1}} \quad (\text{Remember})$$

**Ex.8** In a decomposition reaction, the reaction was found to be 50% complete in 210 seconds when the initial pressure of the mixture was 200 mm. In a second experiment the time of half reaction was 140 seconds when the initial pressure was 300 mm. Calculate the total order of the reaction.

**Sol.** For a  $n^{\text{th}}$  order reaction  $t_{1/2} \propto \frac{1}{c_0^{n-1}}$

$$\frac{210}{140} = \left( \frac{300}{200} \right)^{n-1} \Rightarrow n = 2$$

### 6.4 Ostwald's isolation method :

This method is useful for reactions which involve a large number of reactants. In this method, the concentration of all the reactants are taken in large excess except that of one, so if

$$\text{Rate} = k [A]^a [B]^b [C]^c = k_0 [A]^a$$

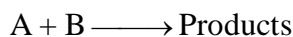
Then value of 'a' can be calculated by previous methods and similarly 'b' and 'c' can also be calculated.

## 6.5 Initial rate method :

For reaction :  $A + B \longrightarrow \text{Products}$

$$\text{Initial rate, } r_0 = K.[A_0]^n [B_0]^m$$

Now, order with respect to A may be determined by comparing the initial rate of reaction at different initial concentration of A but fixed initial concentration of B.

**Ex.9 Consider the following data for the reaction :**

| Run | Initial concentration | Initial concentration | Initial rate (mol s <sup>-1</sup> ) |
|-----|-----------------------|-----------------------|-------------------------------------|
| 1   | 0.10 M                | 1.0 M                 | $2.1 \times 10^{-3}$                |
| 2.  | 0.20 M                | 1.0 M                 | $8.4 \times 10^{-3}$                |
| 3.  | 0.20 M                | 2.0 M                 | $8.4 \times 10^{-3}$                |

**Determine the order of reaction with respect to A and with respect B and the over all order of reaction.**

**Sol.** The rate law may be expressed as :

$$\text{Rate} = k [A]^p [B]^q$$

Comparing experiments 2 and 3

$$(\text{Rate})_2 = k[0.2]^p [1.0]^q = 8.4 \times 10^{-3} \quad (1)$$

$$(\text{Rate})_3 = k[0.2]^p [2.0]^q = 8.4 \times 10^{-3} \quad (2)$$

Dividing equation (2) by (1)

$$\frac{(\text{Rate})_3}{(\text{Rate})_2} = \frac{k[0.2]^p [2.0]^q}{k[0.2]^p [1.0]^q} = \frac{8.4 \times 10^{-3}}{8.4 \times 10^{-3}}$$

$$[2]^q = [1]^0$$

$$\text{or } q = 0$$

Comparing experiments 1 and 2,

$$(\text{Rate})_2 = k[0.20]^p [1.0]^q = 8.4 \times 10^{-3} \quad (3)$$

$$(\text{Rate})_1 = k[0.10]^p [1.0]^q = 2.1 \times 10^{-3} \quad (4)$$

Dividing equation (3) by (4)

$$\frac{(\text{Rate})_2}{(\text{Rate})_1} = \frac{k[0.20]^p [1.0]^q}{k[0.10]^p [1.0]^q} = \frac{8.4 \times 10^{-3}}{2.1 \times 10^{-3}} = 4$$

$$[2]^p = [1]^2 \quad \text{or} \quad p = 2$$

so order with respect to A = 2

order with respect to B = 0

overall order = 2

## 7. APPLICATION OF FIRST ORDER REACTION

(Methods to monitor the progress of the reaction)

### 7.1 Case : 1

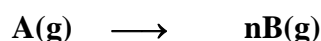
**First order gaseous reaction :**

Progress of gaseous reactions can be monitored by measuring total pressure at a fixed volume & temperature. This method can be applied for those reactions also in which a gas is produced because of decomposition of a solid or liquid. We can get an idea about the concentration of reacting species at a particular time by measuring pressure.

The pressure data can be given in terms of

- (i) Partial pressure of the reactant
- (ii) Total pressure of the reaction system
- (iii) Pressure at only some points of time.

**Ex.10 Find the expression for K in terms of  $P_0$ ,  $P_t$  and n. For the reaction**



**Sol.**  $A(g) \longrightarrow nB(g)$

$$P_0$$

$$P_A = (P_0 - x) \quad nx$$

$$\therefore P_t \text{ (Total pressure at time 't')} = P_0 - x + nx = P_0 + (n - 1)x$$

$$\therefore x = \frac{P_t - P_0}{n - 1}$$

$$\therefore P_A = P_0 - \frac{P_t - P_0}{n - 1} = \frac{P_0 n - P_t}{n - 1}$$

$$\therefore a \propto p_0 \quad \& \quad (a - x) \propto P_A = \frac{nP_0 - P_t}{n - 1}$$

$$\therefore k = \frac{2.303}{t} \log \frac{P_0(n - 1)}{(nP_0 - P_t)}$$

$$\text{Final total pressure after infinite time} = P_f = nP_0$$

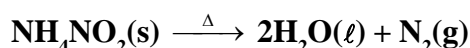
Do not remember the formula but derive it for each question.

### 7.2 Case : 2

**Volume measurement :**

- (i) By measuring the volume of product formed we can monitor the progress of reactions.

**Ex.11 Study of a reaction whose progress is monitored by measuring the volume of a escaping gas.**



**Sol.** Let,  $V_t$  be the volume of  $N_2$  collected at time 't'

$V_{\infty}$  = be the volume of  $N_2$  collected at the end of the reaction.

$$a \propto V_{\infty} \text{ and } x \propto V_t$$

$$(a - x) \propto V_{\infty} - V_t$$

$$\therefore k = \frac{2.303}{t} \log \frac{V_{\infty}}{V_{\infty} - V_t}$$

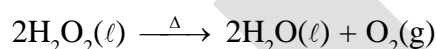
- (ii) **By titration method :** By measuring the volume of titrating agent we can monitor amount of reactant remaining or amount of product formed at any time. It is the **titre value**. Here the milliequivalent or millimoles are calculated using valence factors.

**Ex.12** From the following data show that the decomposition of hydrogen peroxide in aqueous solution is a first - order reaction. What is the value of the rate constant?

| Time in minutes | 0    | 10   | 20   | 30   | 40  |
|-----------------|------|------|------|------|-----|
| Volume V in mL  | 25.0 | 20.0 | 15.7 | 12.5 | 9.6 |

Where V is the volume in mL of standard  $KMnO_4$  solution required to react with a definite volume of hydrogen peroxide solution.

**Sol.** The equation for a first order reaction is,



the volume of  $KMnO_4$  used, evidently corresponds to the undecomposed hydrogen peroxide.

Hence the volume of  $KMnO_4$  used, at zero time corresponds to the initial concentration  $a$  and the volume used after time  $t$ , corresponds to  $(a - x)$  at that time. Inserting these values in the above equation, we get

$$\text{When } t = 10 \text{ min. } k_1 = \frac{2.303}{10} \log \frac{25}{20.0} = 0.022318 \text{ min}^{-1} = 0.000372 \text{ s}^{-1}$$

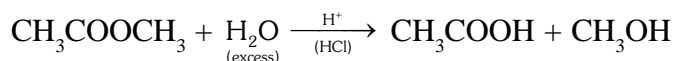
$$\text{When } t = 20 \text{ min. } k_1 = \frac{2.303}{20} \log \frac{25}{15.7} = 0.023265 \text{ min}^{-1} = 0.000387 \text{ s}^{-1}$$

$$\text{When } t = 30 \text{ min. } k_1 = \frac{2.303}{30} \log \frac{25}{12.5} = 0.02311 \text{ min}^{-1} = 0.000385 \text{ s}^{-1}$$

$$\text{When } t = 40 \text{ min. } k_1 = \frac{2.303}{40} \log \frac{25}{9.6} = 0.023932 \text{ min}^{-1} = 0.0003983 \text{ s}^{-1}$$

The constancy of  $k$ , shows that the decomposition of  $H_2O_2$  in aqueous solution is a **first order** reaction. The average value of the rate constant is  $0.0003879 \text{ s}^{-1}$ .

**Ex.13 Study of acid hydrolysis of an ester.**



The progress of this reaction is monitored or determined by titrating the fixed volume of reaction mixture at different time intervals against a standard solution of NaOH using phenolphthalein as indicator. Find out rate constant of the reaction in terms of volume of NaOH consumed at  $t = 0$ ,  $V_0$ , at  $t = \infty$ ,  $V_\infty$  & at time  $t$ ,  $V_t$ .

**Sol.** Let,  $V_0$  = Volume of NaOH used at  $t = 0$  [this is exclusively for HCl.]

$V_t$  = Volume of NaOH used at 't'

$V_\infty$  = Volume of NaOH used at  $t = \infty$

$$a \propto (V_\infty - V_0)$$

$$(a - x) \propto (V_\infty - V_t)$$

$$x \propto (V_t - V_0)$$

$$k = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}$$

**7.3 Case : 3**

**Optical rotation measurement :**

It is used for optically active sample. It is applicable if there is at least one optically active species involved in chemical reaction.

- The optically active species may be present in reactant or product.

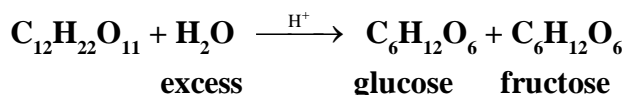
It is found that  $(r_\infty - r_0) \propto a$  ( $a$  = concentration,  $x$  = amount consumed)

$$(r_\infty - r_t) \propto (a - x)$$

Where are  $r_0$ ,  $r_t$ ,  $r_\infty$  are angle of optical rotation at time  $t = 0$ ,  $t = t$  and  $t = \infty$ .

$$k = \frac{2.303}{t} \log \frac{r_\infty - r_0}{r_\infty - r_t} \quad (\text{Remember})$$

**Ex.14 Study of hydrolysis of sucrose, progress of this reaction is monitored with the help of polarimeter because a solution of sucrose is dextrorotatory and on hydrolysis, the mixture of glucose and fructose obtained becomes laevorotatory. That's why this reaction is also known as inversion of cane sugar.**



Let the readings in the polarimeter be

$t = 0$ ,  $\theta_0$ ;  $t = 't'$ ,  $\theta_t$  and at  $t = \infty$ ,  $\theta_\infty$

Then calculate rate constant 'k' in terms of these readings.



**Sol.** The principle of the experiment is that change in the rotation is directly proportional to the amount of sugar hydrolysed.

$$\therefore a \propto (\theta_0 - \theta_\infty) \quad ; \quad (a - x) \propto (\theta_t - \theta_\infty) ; x \propto (\theta_0 - \theta_t)$$

$$k = \frac{2.303}{t} \log \left( \frac{\theta_0 - \theta_\infty}{\theta_t - \theta_\infty} \right)$$

#### 7.4 Case : 4

##### First order growth reaction :

For bacteria multiplication or virus growth use following concept

Consider a growth reaction,

**Time** **Population (or colony)**

|   |         |
|---|---------|
| 0 | a       |
| t | (a + x) |

$$\frac{dx}{dt} = k(a + x) \quad \text{or} \quad \frac{dx}{(a + x)} = k dt$$

On integration

$$\log_e (a + x) = kt + C \quad \text{at} \quad t = 0 ; x = 0 \Rightarrow C = \log_e a$$

$$kt = -\log_e \frac{a}{(a + x)} = -\frac{2.303}{t} \log_{10} \left( \frac{a}{(a + x)} \right)$$

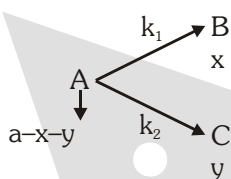
$$k = \frac{2.303}{t} \log_{10} \left( \frac{a + x}{a} \right)$$

❖ **Generation time :**

$$\text{At } t = \text{generation time, } x = a \quad \therefore \quad t = \frac{0.693}{K}$$

#### 8. SOME SPECIAL CASES :

##### 8.1 FIRST ORDER PARALLEL OR COMPETING OR SIMULTANEOUS REACTIONS



$$\text{At } t = 0 \quad [A] = a \quad [B] = [C] = 0$$

(i) **Differential rate law :**

$$\frac{d[B]}{dt} = k_1 [A] ; \quad \frac{d[C]}{dt} = k_2 [A]$$

$$\text{and, } \frac{-d[A]}{dt} = \frac{d[B]}{dt} + \frac{d[C]}{dt} \Rightarrow \frac{-d[A]}{dt} = (k_1 + k_2) [A] = k_{\text{eff}} [A]$$

$$k_{\text{eff}} = k_1 + k_2 = \text{overall rate constant for the disappearance of 'A'}$$

(ii) **Integral rate law :**

$$[A]_t = ae^{-k_{\text{eff}} t} = ae^{-(k_1 + k_2)t}$$

$$\frac{d[B]}{dt} = k_1 [A] \Rightarrow \frac{d[B]}{dt} = k_1 a e^{-(k_1 + k_2)t}$$

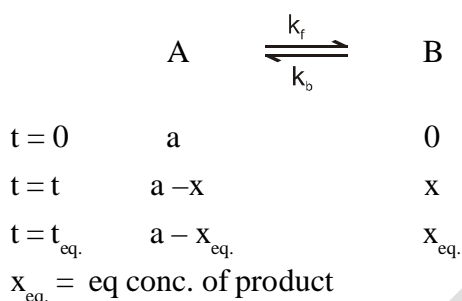
$$[B] = \left( \frac{k_1 a}{k_1 + k_2} \right) (1 - e^{-(k_1 + k_2)t})$$

$$\text{Similarly, } [C] = \left[ \frac{k_2 a}{k_1 + k_2} \right] (1 - e^{-(k_1 + k_2)t})$$

(iii) **Composition of product :**

$$\frac{[B]}{[C]} = \frac{k_1}{k_2}$$

## 8.2 FIRST ORDER REVERSIBLE REACTION



(i)  $\frac{d[A]}{dt} = \frac{d[B]}{dt} = 0$  ( $\because$  At equilibrium, conc. will not changed)

(ii)  $\frac{d[A]}{dt} = -k_f[A] + k_b[B] \Rightarrow \frac{d[B]}{dt} = -k_b[B] + k_f[A]$

$$\frac{d(a-x)}{dt} = -k_f(a-x) + k_b x$$

$$-\frac{dx}{dt} = -k_f a + (k_f + k_b)x$$

$$\text{At eq}^m, \frac{dx}{dt} = 0 = k_f a + (k_f + k_b)x_{eq}$$

$$k_f a = (k_f + k_b)x_{eq}$$

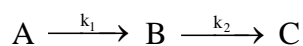
$$-\frac{dx}{dt} = -(k_f + k_b)x_{eq} + (k_f + k_b)x$$

$$\frac{dx}{dt} = (k_f + k_b)(x_{eq} - x)$$

$$\int_0^x \frac{dx}{(x_{eq} - x)} = (k_f + k_b) \int_0^t dt$$

$$k_f + k_b = \frac{1}{t} \ln \left( \frac{x_{eq.}}{x_{eq.} - x} \right) \text{ (No need to remember this equation)}$$

## 8.3 FIRST ORDER SEQUENTIAL REACTION



All first order reactions

|       |       |   |   |
|-------|-------|---|---|
| t = 0 | a     | 0 | 0 |
| t = t | a - x | y | z |

(i) For 'A'

$$\frac{-d[A]}{dt} = r_1 = k_1 [A]$$

$$\frac{-d[A]}{[A]} = k_1 dt$$

$$[A]_t = [A]_0 e^{-k_1 t}$$

$$a - x = a e^{-k_1 t}$$

$$x = a (1 - e^{-k_1 t})$$

(ii) For 'B'

$$\frac{dy}{dt} = k_1 a e^{-k_1 t} - k_2 y$$

$$\frac{dy}{dt} + k_2 y = k_1 a e^{-k_1 t}$$

$$dy + k_2 y dt = k_1 a e^{-k_1 t} dt$$

$$e^{k_2 t} dy + k_2 y e^{k_2 t} = k_1 a e^{-k_1 t} \cdot e^{k_2 t} dt$$

$$\int_0^t d(k_2 y e^{k_2 t}) = \int_0^t k_1 a e^{(k_2 - k_1)t} dt$$

$$k_2 y e^{k_2 t} = \left( \frac{k_1 a}{k_2 - k_1} \right) e^{(k_2 - k_1)t} + y \quad (\text{No need to remember})$$

(iii) Calculate time at which concentration of B will be maximum.

$$\frac{dy}{dt} = 0$$

$$-k_1 e^{-k_1 t} + k_2 e^{-k_2 t} = 0$$

$$e^{-k_2 t} = \frac{k_1}{k_2} e^{-k_1 t}$$

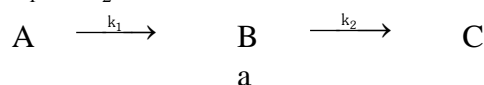
$$e^{k_1 t} = \frac{k_1}{k_2} e^{k_2 t} \Rightarrow k_1 t = \ln \frac{k_1}{k_2} + k_2 t$$

$$t_{\max.} = \frac{1}{(k_1 - k_2)} \ln \frac{k_1}{k_2}$$

$$(iv) [B]_{\max} = a \times \left[ \frac{k_2}{k_1} \right]^{\frac{k_2}{k_1 - k_2}} = [A_0] \left[ \frac{k_2}{k_1} \right]^{\frac{k_2}{k_1 - k_2}}$$

### 8.3.1 Case -I

$$k_1 \gg k_2$$



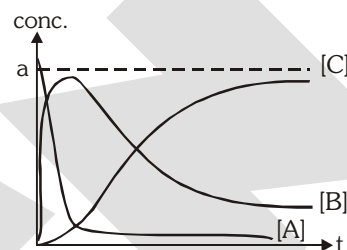
$\left[ \begin{array}{c} \text{Tends to zero} \\ \text{very fast} \end{array} \right]$

$$a \quad a - x \quad x$$

$$[A] = ae^{-k_1 t}$$

$$[B] = ae^{-k_2 t}$$

$$[C] = a(1 - e^{-k_2 t})$$



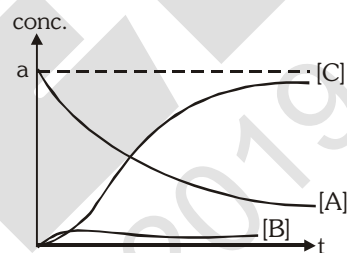
### 8.3.2 Case -II

$$k_2 \gg k_1$$

$$[B]_t \rightarrow 0$$

$$[A] = ae^{-k_1 t}$$

$$[C] = a(1 - e^{-k_1 t})$$



**Note :** Both Case (I) and Case (II) show that rate of overall reaction depends on rate of slowest step (RDS.)

## 9. EFFECT OF TEMPERATURE ON RATE OF REACTION :

In early days the effect of temperature on reaction rate was expressed in terms of **temperature coefficient** ( $\mu$ ) which was defined as the ratio of rate of reaction at two different temperature differing by  $10^\circ\text{C}$  (usually these temperatures were taken as  $25^\circ\text{C}$  and  $35^\circ\text{C}$ )

$$\text{T.C, } \mu = \frac{K_{T+10}}{K_T} \approx 2 \text{ to } 3 \quad (\text{for most of the reactions})$$

**Exception :** For some reactions, temperature coefficient is also found to be less than unity.

For example,  $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$  rate of reaction decreases on increasing temperature.

**Note :** Rate of reaction increases on increasing temperature (Generally ;  $\text{T.C} > 1$ )

**Ex.15** For a reaction T.C. = 2, Calculate  $\frac{k_{40^\circ\text{C}}}{k_{25^\circ\text{C}}}$  for this reaction. Assuming T.C remains constant.

**Sol.**  $\frac{k_2}{k_1} = (\text{T.C.})^{\frac{\Delta t}{10}} = (2)^{\frac{15}{10}} = (2)^{\frac{3}{2}} = \sqrt{8}$

But the method of temperature coefficient was not exact to explain the effect of temperature on reaction rate. For that a new theory was evolved.

### 9.1 Collision theory of reaction rate :

It was developed by **Max Trautz** and **William Lewis**. It gives insight in to the energetics and mechanistic aspects of reactions.

It is based upon kinetic theory of gases.

**According to this theory :**

- (i) A chemical reaction takes place due to the collision among reactant molecules. The number of collisions taking place per second per unit volume of the reaction mixture is known as collision frequency (Z).
- (ii) Every collision does not bring a chemical change. The collision that actually produce the products are effective collision. For a collision to be effective the following two barriers are to be cleared.

❖ **Energy barrier :** The minimum amount of absolute energy which the colliding molecules must possess as to make the chemical reaction to occur is known as **threshold energy**.

- Reactant molecules having energy equal or greater than the threshold are called **active molecules** and those having energy less than the threshold are called **passive molecules**.
- At a given temperature there exists a dynamic equilibrium between active and passive molecules. The process of transformation from passive to active molecules being endothermic, increase of temperature increases the number of active molecules and hence the reaction.

**Passive molecules  $\rightleftharpoons$  Active molecules,  $\Delta H = +ve$**

- “The minimum amount of excess energy required by reactant molecules to participate in a reaction is called **activation energy ( $E_a$ )**”.

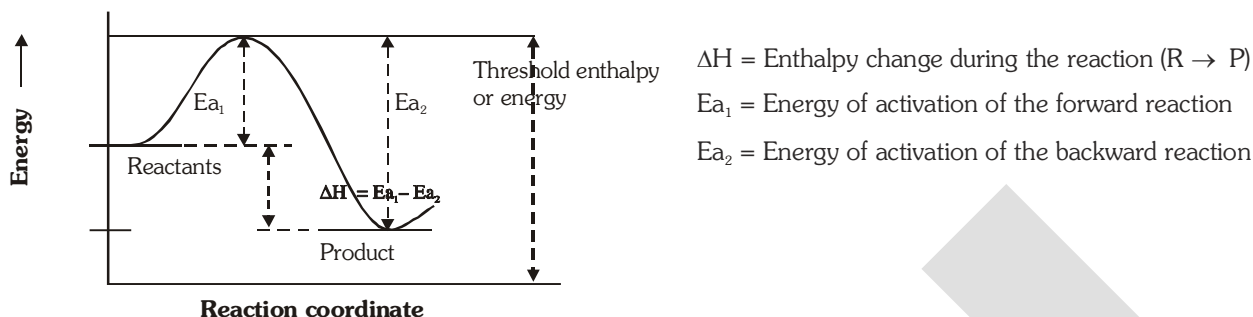
### CONCEPT OF ENERGY OF ACTIVATION ( $E_a$ ) :

- The average extra amount of energy which the reactant molecules (having energy less than the threshold) must acquire so that their mutual collision may lead to the breaking of bond(s) and hence the energy is known as energy of activation of the reaction. It is denoted by the symbol  $E_a$ .  
Thus,

**$E_a$  = Threshold energy – Actual average energy of reactants**

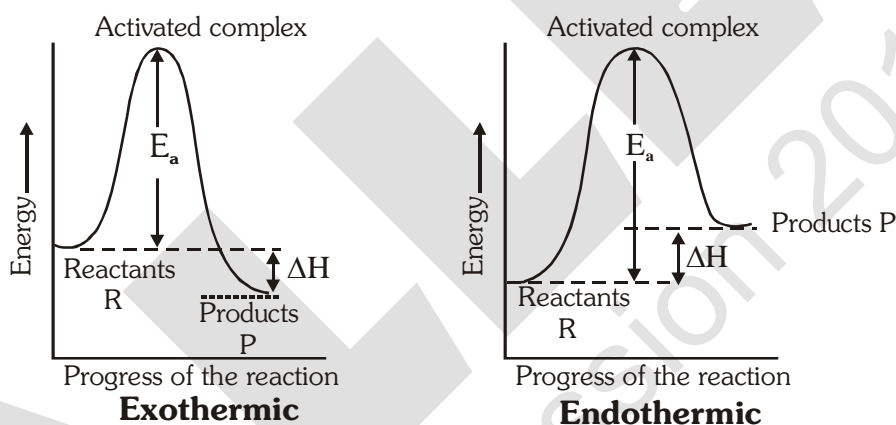
**$E_a$  is expressed in  $\text{kcal mole}^{-1}$  or  $\text{kJ mole}^{-1}$ .**

- The essence of Collision Theory of reaction rate is that there exists an energy barrier in the reaction path between reactant(s) and product(s) and for reaction to occur, the reactant molecules must climb over the top of the barrier which they do by collision. The existence of energy barrier and concept of  $E_a$  can be understood from the following diagram.



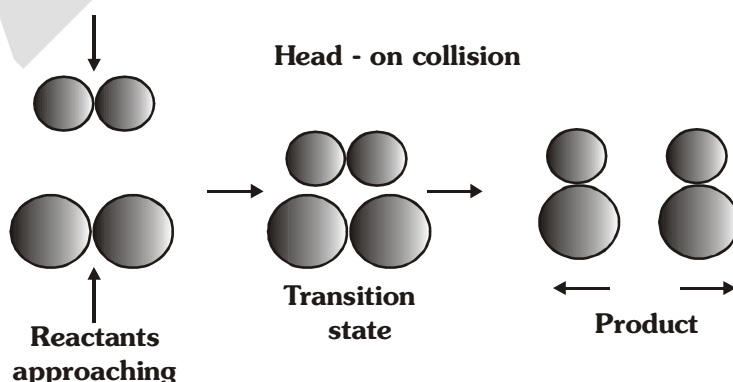
From the figure above it can be concluded that the minimum activation energy of any exothermic reaction will be zero while minimum activation energy for any endothermic reaction will be equal to  $\Delta H$ .

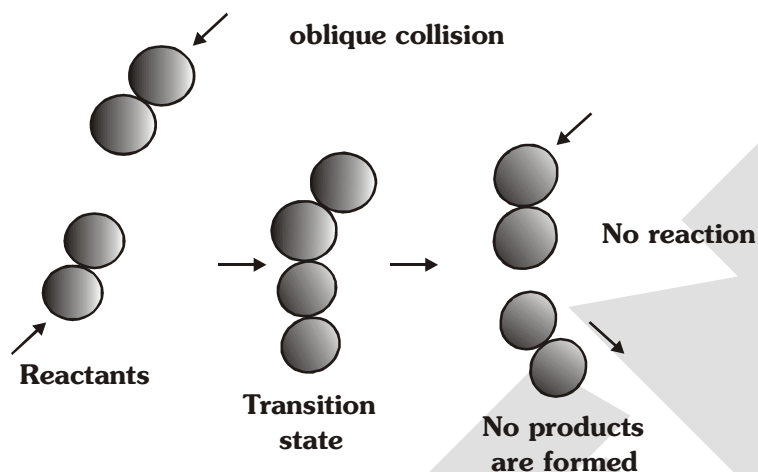
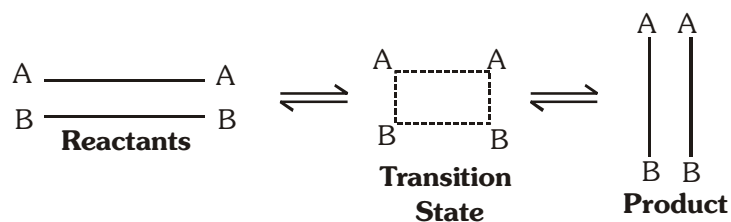
Greater the height of energy barrier, greater will be the energy of activation and more slower will be the reaction at a given temperature.



- ❖ **Orientation barrier :** Energy alone does not determine the effectiveness of the collision. The reacting molecules must collide in proper direction to make collision effective. Following diagrams can explain importance of suitable direction for collision.

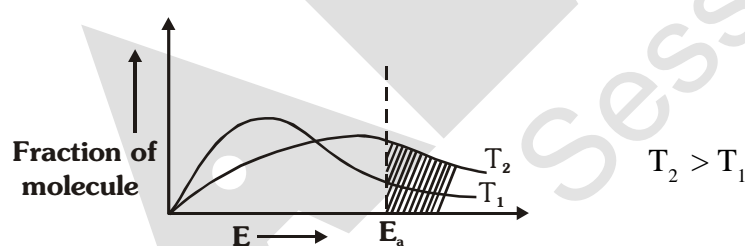
Consider reaction :  $A_2 + B_2 \rightarrow 2AB$





- (iii) **Rate of any chemical reaction** = Collision frequency  $\times$  fraction of the total number of effective collision.  
 = Collision frequency  $\times$  fraction of the total number of collision in which K.E. of the colliding molecules equals to  $E_a$  or exceeds over it  $\times$  fraction of collision in proper orientation.

From Maxwellian distribution, it is found that fraction of molecules having excess energy greater than threshold energy lead to the formation of product.



$e^{-E_a/RT} \rightarrow$  Represents fraction of molecules having K.E. greater than or equal to  $E_a$ .

$$\text{Rate} \propto e^{-E_a/RT}$$

Dependence of rate on temperature is due to dependence of  $k$  on temperature.

$$k \propto e^{-E_a/RT}$$

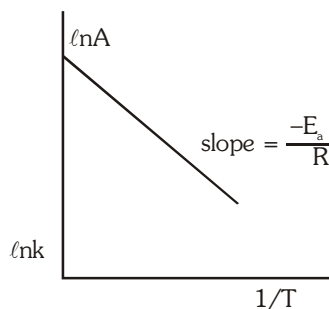
$$k = Ae^{-E_a/RT}$$

**[Arrhenius equation]**

'A' is **pre-exponential** factor or **frequency factor** representing collisions taking place with proper orientation. A and  $E_a$  are assumed to be independent of temperature.

$$\ln k = \ln A - \frac{E_a}{RT}$$

As  $T \rightarrow \infty$ ,  $k \rightarrow A$



At temperature  $T_1$ , Rate constant =  $k_1$

At temperature  $T_2$ , Rate constant =  $k_2$

$$\ln k_1 = \ln A - \frac{E_a}{RT_1} \quad \& \quad \ln k_2 = \ln A - \frac{E_a}{RT_2} \Rightarrow \ln \frac{k_2}{k_1} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

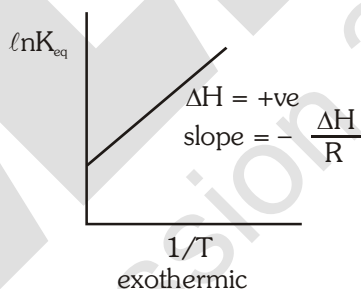
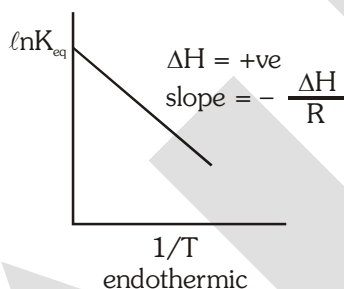
## 9.2 REVERSIBLE REACTIONS

$$k_f = A_f e^{-E_{af}/RT}$$

$$k_b = A_b e^{-E_{ab}/RT}$$

$$K_{eq} = \frac{k_f}{k_b} = \frac{A_f}{A_b} \frac{e^{-E_{af}/RT}}{e^{-E_{ab}/RT}} = \left( \frac{A_f}{A_b} \right) e^{-(E_{af} - E_{ab})/RT}$$

$$\ln K_{eq} = -\frac{\Delta H}{RT} + \ln \left( \frac{A_f}{A_b} \right)$$



**Ex.16** For a reaction, temperature coefficient = 2, then calculate the activation energy (in kJ) of the reaction.

**Sol.** Given : Temperature coefficient =  $\frac{K_2}{K_1} = 2$

$$T_1 = 25 + 273 = 298 \text{ K}$$

$$T_2 = 35 + 273 = 308 \text{ K}$$

$$\log \frac{K_2}{K_1} = \frac{E_a}{2.303R} \left( \frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\log 2 = \frac{E_a}{2.303 \times 8.314} \times \left( \frac{10}{298 \times 308} \right)$$

$$E_a = 52.31 \text{ kJ mol}^{-1}$$



**Ex.17** For first order gaseous reaction,  $\log k$  when plotted against  $\frac{1}{T}$ , it give a straight the with a slope of  $-8000$ . Calculate the activation energy of the reaction.

**Sol.** For an arrhenius equation  $k = Ae^{-E_a/RT}$

$$\log k = \log A - \frac{E_a}{2.303R} \times \frac{1}{T}$$

when curve is plotted between  $\log k$  and  $\frac{1}{T}$ . A straight line is obtained and a slope of this curve

$$= -\frac{E_a}{2.303R}$$

$$\text{Then, } \frac{E_a}{2.303R} = 8000$$

$$\text{or } E_a = 8000 \times 2.303 \times 2 = 36848 \text{ calories}$$

**Ex.18** The slope of the plot of  $\log k$  vs  $\frac{1}{T}$  for a certain reaction was found to be  $-5.4 \times 10^3$ . Calculate the energy of activation of the reaction. If the rate constant of the reaction is  $1.155 \times 10^{-2} \text{ sec}^{-1}$  at  $373 \text{ K}$ , what is its frequency factor ?

**Sol.** (a)  $\text{Slope} = \frac{-E}{2.303 R} = -5.4 \times 10^3$

$$E_a = 5.4 \times 10^3 \times 2.303 \times 1.987$$

$$= 24.624 \text{ cal mol}^{-1}$$

(b)  $K = Ae^{-E/RT}$ ;  $\log 1.155 \times 10^{-2} = \log A - \frac{24.624}{2.303 \times 1.987 \times 373}$

$$\text{or } A = 1.764 \times 10^3 \text{ sec}^{-1}$$

## 10. CATALYST AND CATALYSIS :

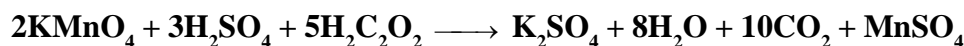
A catalyst is a substance, which increases the rate of a reaction without itself being consumed at the end of the reaction, and the phenomenon is called **catalysis**.

Thermal decomposition of  $\text{KClO}_3$  is found to be accelerated by the presence of  $\text{MnO}_2$ . Here  $\text{MnO}_2$  acts as a catalyst.



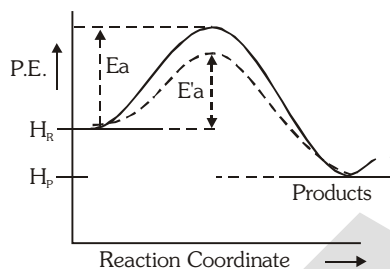
- $\text{MnO}_2$  can be received in the same composition and mass at the end of the reaction.
- The word catalyst should not be used when the added substance reduces the rate of reaction. The substance is then called **inhibitor**.
- Catalyst are generally foreign substances but sometimes one of the product may act as a catalyst and such catalyst is called "**auto catalyst**" and the phenomena is called **auto catalysis**.

In the permanganate titration of oxalic acid initially there is slow discharge of the colour of permanganate solution but afterwards the discharge of the colour become faster. This is due to the formation of  $\text{MnSO}_4$  during the reaction which acts as a catalyst for the same reaction. Thus,  $\text{MnSO}_4$  is an "**auto catalyst**" for this reaction. This is an example of auto catalyst.



### 10.1 General characteristics of catalyst :

- A catalyst does not initiate the reaction normally. It simply fastens it.
- Only a small amount of catalyst can catalyse the reaction.
- A catalyst does not alter the position of equilibrium i.e. magnitude of equilibrium constant and hence  $\Delta G^\circ$ . It simply lowers the time needed to attain equilibrium. This means if a reversible reaction in absence of catalyst completes to go to the extent of 75% till attainment of equilibrium, and this state of equilibrium is attained in 20 minutes then in presence of a catalyst, the reaction will still go to 75% of completion on the attainment of equilibrium but the time needed for this will be less than 20 minutes.

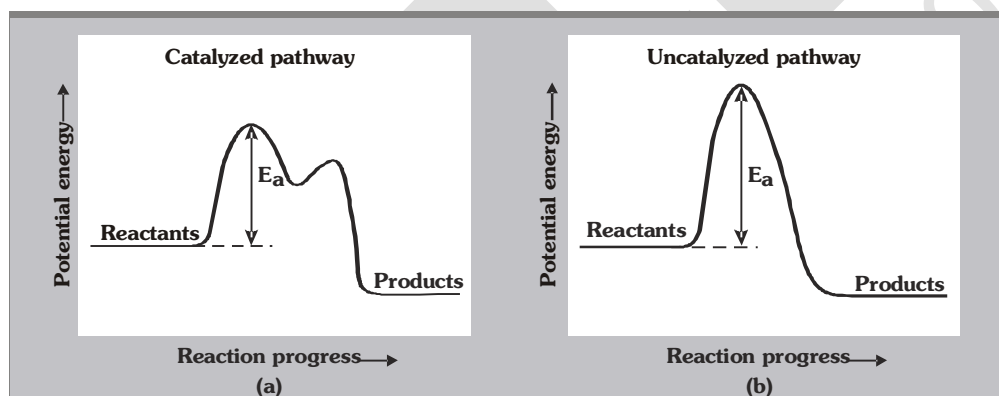


A catalyst drives the reaction through a low energy path and hence  $E_a$  is less. That is, the function of the catalyst is to lower down the activation energy.

$E_a$  = Energy of activation in absence of catalyst.

$E'_a$  = Overall Energy of activation in presence of catalyst.

$E_a - E'_a$  = Lowering of activation energy by catalyst.



### 10.2 Comparison of rates of reaction in presence and absence of catalyst :

If  $k$  and  $k_{cat}$  be the rate constant of a reaction at a given temperature  $T$ ,  $E_a$  and  $E'_a$  are the activation energies of the reaction in absence and presence of catalyst, respectively, the

$$\frac{k_{cat}}{k} = \frac{Ae^{-E'_a/RT}}{Ae^{-E_a/RT}} = Ae^{(E_a - E'_a)/RT}$$

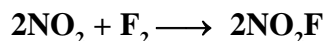
Since  $E_a - E'_a$  is positive so  $k_{cat} > k$ . the ratio  $\frac{k_{cat}}{k}$  gives the number of times the rate of reaction will increase by the use of catalyst at a given temperature.

The rate of reaction in the presence of catalyst at any temperature  $T_1$  may be made equal to the rate of reaction in absence of catalyst but for this sake we will have to raise the temperature. Let this

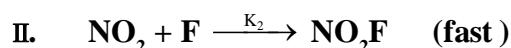
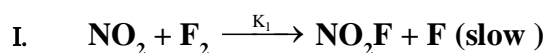
temperature be  $T_2 = e^{-E'_a/RT_1} = e^{-E_a/RT_2}$  or  $\frac{E'_a}{T_1} = \frac{E_a}{T_2}$

## 11 CALCULATION OF RATE LAW / ORDER

11.1 When first step is rate determining step.

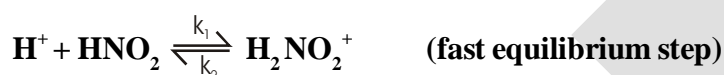
**Ex.19** Calculate order and rate law of reaction -

with help of mechanism

**Sol.** According to RDS

$$\text{Rate} = k_1 [\text{NO}_2] [\text{F}_2]$$

11.2 Equilibrium approach :

**Ex.20** For the reaction,  $\text{H}^+ + \text{HNO}_2 + \text{C}_6\text{H}_5\text{NH}_2 \xrightarrow{\text{Br}^-} \text{C}_6\text{H}_5\text{N}_2^+ + 2\text{H}_2\text{O}$ , the mechanism is,

intermediate



Derive the rate law expression for the reaction

**Sol.**  $r = k_3 [\text{Br}^-] [\text{H}_2\text{NO}_2^+]$ 

$$K_{\text{eq}} = \frac{k_1}{k_2} = \frac{[\text{H}_2\text{NO}_2^+]}{[\text{H}^+][\text{HNO}_2]}$$

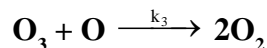
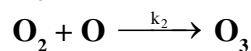
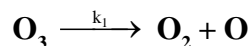
$$[\text{H}_2\text{NO}_2^+] = \left[ \frac{k_1}{k_2} \right] [\text{H}^+] [\text{HNO}_2]$$

$$r = \frac{k_1 k_3}{k_2} [\text{H}^+] [\text{HNO}_2] [\text{Br}^-].$$

**Note :** Rate law can have reactant product or catalyst concentration terms but not any intermediate terms.

11.3 CASE-III : STEADY STATE APPROXIMATION :

Ex.21 For the reaction,  $2\text{O}_3 \rightarrow 3\text{O}_2$ , the mechanism is



Derive the rate law expression for the reaction

Sol.  $\text{rate} = -\frac{1}{2} \frac{d[\text{O}_3]}{dt} = \frac{1}{3} \frac{d[\text{O}_2]}{dt}$

$$\frac{d[\text{O}_3]}{dt} = -k_1 [\text{O}_3] + k_2 [\text{O}_2][\text{O}] - k_3 [\text{O}_3][\text{O}]$$

$$\frac{d[\text{O}_2]}{dt} = k_1 [\text{O}_3] - k_2 [\text{O}_2][\text{O}] + k_3 [\text{O}_3][\text{O}]$$

At steady state  $\frac{d[\text{O}]}{dt} = 0$

$$\frac{d[\text{O}]}{dt} = k_1 [\text{O}_3] - k_2 [\text{O}_2][\text{O}] - k_3 [\text{O}_3][\text{O}] = 0$$

$$[\text{O}] = \frac{k_1 [\text{O}_3]}{k_2 [\text{O}_2] + k_3 [\text{O}_3]}$$

$$\frac{d[\text{O}_3]}{dt} = -k_1 [\text{O}_3] + \frac{\{k_2 [\text{O}_2] - k_1 [\text{O}_3]\}}{k_2 [\text{O}_2] + k_3 [\text{O}_3]} \cdot \frac{k_1 k_3 [\text{O}_3]^2}{k_2 [\text{O}_2] + k_3 [\text{O}_3]}$$

$$= -k_1 [\text{O}_3] + \frac{k_1 k_2 [\text{O}_2] [\text{O}_3] - k_1 k_3 [\text{O}_3]^2}{k_2 [\text{O}_2] + k_3 [\text{O}_3]}$$

$$= \frac{k_1 k_2 [\text{O}_2] [\text{O}_3] - k_1 k_3 [\text{O}_3]^2 + k_1 k_2 [\text{O}_2] [\text{O}_3] - k_1 k_3 [\text{O}_3]^2}{k_2 [\text{O}_2] + k_3 [\text{O}_3]}$$

$$= \frac{-2k_1 k_3 [\text{O}_3]^2}{k_2 [\text{O}_2] + k_3 [\text{O}_3]}$$

$$\left[ -\frac{1}{2} \frac{d}{dt} [\text{O}_3] \right] = \frac{k_1 k_3 [\text{O}_3]^2}{k_2 [\text{O}_2] + k_3 [\text{O}_3]}$$

$$\text{Rate} = -\frac{1}{2} \frac{d}{dt} [\text{O}_3]$$

$$\text{So, Rate (r)} = \frac{k_1 k_3 [\text{O}_3]^2}{k_2 [\text{O}_2] + k_3 [\text{O}_3]}$$

if 3<sup>rd</sup> step is RDS then  $k_1 \gg k_3$   
 $k_2 \gg k_3$

$$\text{Rate (r)} = \frac{k_1 k_3}{k_2} [\text{O}_3]^2 [\text{O}_2]^{-1} \text{ (ie. first order)}$$

## MISSLENIIOUS PREVIOUS YEARS QUESTION

1. Which of the following statement(s) is (are) correct [JEE 1999]  
 (A) A plot of  $\log K_p$  versus  $1/T$  is linear  
 (B) A plot of  $\log [X]$  versus time is linear for a first order reaction,  $X \longrightarrow P$   
 (C) A plot of  $\log P$  versus  $1/T$  is linear at constant volume.  
 (D) A plot of  $P$  versus  $1/V$  is linear at constant temperature.

Ans. (A,B,D)

2. The rate constant for an isomerisation reaction  $A \rightarrow B$  is  $4.5 \times 10^{-3} \text{ min}^{-1}$ . If the initial concentration of A is 1 M. Calculate the rate of the reaction after 1 h. [JEE 1999]

Ans.  $3.435 \times 10^{-3} \text{ M/min}$

Sol.  $r = k[A]$

$$r = K[A]_0 e^{-kt}$$

$$r = (4.5 \times 10^{-3}) e^{-4.5 \times 10^{-3} \times 60} \text{ M/min.}$$

3. A hydrogenation reaction is carried out at 500 K. If the same reaction is carried out in the presence of a catalyst at the same rate, the temperature required is 400 K. Calculate the activation energy of the reaction if the catalyst lowers the activation barrier by  $20 \text{ kJmol}^{-1}$ . [JEE 2000]

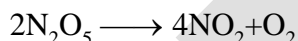
Ans.  $100 \text{ kJmol}^{-1}$

Sol.  $\ln \left( \frac{r_2}{r_1} \right) = -\frac{1}{R} \left( \frac{E_{a2}}{T_2} - \frac{E_{a1}}{T_1} \right)$

$$\ln (1) = -\frac{1}{R} \left( \frac{E_{a1} - 20}{400} - \frac{E_{a1}}{500} \right)$$

$$E_{a1} = 100$$

4. The rate constant for the reaction [JEE SCR 2000]



is  $3.0 \times 10^{-5} \text{ sec}^{-1}$ . if the rate is  $2.4 \times 10^{-5} \text{ mol litre}^{-1} \text{ sec}^{-1}$ , then the concentration of  $\text{N}_2\text{O}_5$  (in  $\text{mol litre}^{-1}$ ) is

- (A) 1.4 (B) 1.2 (C) 0.004 (D) 0.8

Ans. (D)

Sol.  $r = k[\text{N}_2\text{O}_5]^2$

$$2.4 \times 10^{-5} = 3 \times 10^{-5} [\text{N}_2\text{O}_5]^2$$

5. If I is the intensity of absorbed light and C is the concentration of AB for the photochemical process :  $\text{AB} + h\nu \longrightarrow \text{AB}$ , the rate of formation of AB is directly proportional to [JEE SCR 2001]

- (A) C (B) I (C)  $I^2$  (D) CI

Ans. (B)

Sol. For phot chemical reaction

$$r \propto I$$

6. The rate of a first order reaction is  $0.04 \text{ mole litre}^{-1} \text{ s}^{-1}$  at 10 minutes and  $0.03 \text{ mol litre}^{-1} \text{ s}^{-1}$  at 20 minutes after initiation. Find the half life of the reaction. [JEE 2001]

Ans.  $t_{1/2} = 24.14 \text{ min}$

Sol.  $\left( \frac{\ln 2}{t_{1/2}} \right) (20 - 10) = \ln \left( \frac{0.04}{0.03} \right)$

7. Consider the chemical reaction,  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$ . The rate of this reaction can be expressed in term of time derivative of concentration of  $\text{N}_2(\text{g})$ ,  $\text{H}_2(\text{g})$  or  $\text{NH}_3(\text{g})$ . Identify the correct relationship amongst the rate expressions. [JEE SCR 2002]

- (A)  $\text{Rate} = -\frac{d[\text{N}_2]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt}$   
 (B)  $\text{Rate} = -\frac{d[\text{N}_2]}{dt} = -3 \frac{d[\text{H}_2]}{dt} = 2 \frac{d[\text{NH}_3]}{dt}$   
 (C)  $\text{Rate} = \frac{d[\text{N}_2]}{dt} = \frac{1}{3} \frac{d[\text{H}_2]}{dt} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt}$   
 (D)  $\text{Rate} = -\frac{d[\text{N}_2]}{dt} = -\frac{d[\text{H}_2]}{dt} = \frac{d[\text{NH}_3]}{dt}$

Ans. (A)

Sol. 
$$\frac{-d[\text{N}_2]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt}$$

8. In a first order reaction the concentration of reactant decreases from  $800 \text{ mol/dm}^3$  to  $50 \text{ mol/dm}^3$  in  $2 \times 10^4 \text{ sec}$ . The rate constant of reaction in  $\text{sec}^{-1}$  is [JEE SCR 2003]

- (A)  $2 \times 10^4$  (B)  $3.45 \times 10^{-5}$   
 (C)  $1.3486 \times 10^{-4}$  (D)  $2 \times 10^{-4}$

Ans. (C)

Sol. 
$$K(2 \times 10^4) = \ln \left( \frac{800}{50} \right)$$

9. The reaction,  $\text{X} \longrightarrow \text{Product}$  follows first order kinetics. In 40 minutes the concentration of X changes from  $0.1 \text{ M}$  to  $0.025 \text{ M}$ . Then the rate of reaction when concentration of X is  $0.01 \text{ M}$

- (A)  $1.73 \times 10^{-4} \text{ M min}^{-1}$  (B)  $3.47 \times 10^{-5} \text{ M min}^{-1}$   
 (C)  $3.47 \times 10^{-4} \text{ M min}^{-1}$  (D)  $1.73 \times 10^{-5} \text{ M min}^{-1}$

[JEE SCR 2004]

Ans. (C)

Sol. 
$$K(40) = \ln \left( \frac{0.1}{0.025} \right)$$

$$K = \frac{\ln 2}{20}$$

$$r = K[X]$$

$$= \frac{\ln 2}{20} \times 0.1$$

10.  $2\text{X}(\text{g}) \longrightarrow 3\text{Y}(\text{g}) + 2\text{Z}(\text{g})$

|                                     |     |     |     |
|-------------------------------------|-----|-----|-----|
| Time (in Min)                       | 0   | 100 | 200 |
| Partial pressure of X (in mm of Hg) | 800 | 400 | 200 |

Assuming ideal gas condition. Calculate

- (a) Order of reaction  
 (b) Rate constant ( $K_x$ )  
 (c) Time taken for 75% completion of reaction  
 (d) Total pressure when  $P_x = 700 \text{ mm}$ .

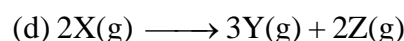
[JEE 2005]

**Ans.** (a) 1, (b)  $6.93 \times 10^{-3} \text{ min}^{-1}$ , (c) 200, (d) 950 mm

**Sol.** (a) As half life is constant so it will be of first order.

$$(b) K_x(100) = \ln \left( \frac{800}{400} \right)$$

$$(c) t = 75\% = 2t_{50\%} = 2 \left( \frac{\ln 2}{K_x} \right)$$



$$800 - x \quad \frac{3x}{2} \quad x$$

$$\text{Here } x = 100$$

$$\text{So } P_T = 800 + \frac{3x}{2} = 950$$

**11.** Which of the following statement is incorrect about order of reaction?

[JEE 2005]

- (A) Order of reaction is determined experimentally
- (B) It is the sum of power of concentration terms in the rate law expression
- (C) It does not necessarily depend on stoichiometric coefficients
- (D) Order of the reaction can not have fractional value.

**Ans.** (D)

**12.** Consider a reaction  $aG + bH \rightarrow \text{Products}$ . When concentration of both the reactants G and H is doubled, the rate increases by eight times. However, when concentration of G is doubled keeping the concentration of H fixed, the rate is doubled. The overall order of the reaction is :

[JEE 2006]

- (A) 0 (B) 1 (C) 2 (D) 3

**Ans.** (D)

**Sol.**  $\frac{r_2}{r_1} = \left( \frac{[G]_2}{[G]_1} \right)^\alpha \left( \frac{[H]_2}{[H]_1} \right)^\beta$

$$8 = 2^\alpha \cdot 2^\beta \quad \dots\dots(1)$$

$$2 = 2^\alpha \quad \dots\dots(2)$$

$$\alpha = 1, \beta = 2$$

**13.** Under the same reaction conditions, initial concentration of  $1.386 \text{ mol dm}^{-3}$  of a substance becomes half in 40 seconds and 20 seconds through first order and zero order kinetics, respectively. Ratio

$\left( \frac{k_1}{k_0} \right)$  of the rate constants for first order ( $k_1$ ) and zero order ( $k_0$ ) of the reactions is [JEE 2008]

- (A)  $0.5 \text{ mol}^{-1} \text{ dm}^3$  (B)  $1.0 \text{ mol dm}^{-3}$   
(C)  $1.5 \text{ mol dm}^{-3}$  (D)  $2.0 \text{ mol}^{-1} \text{ dm}^3$

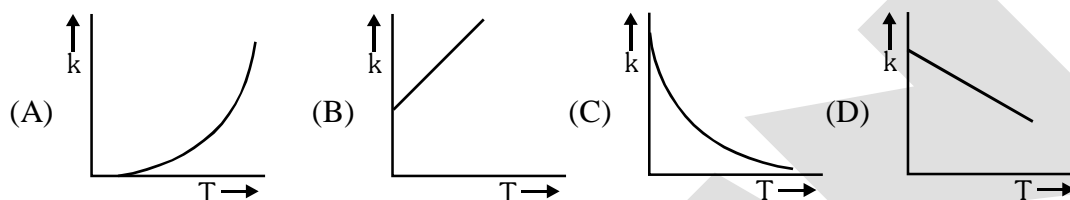
**Ans.** (A)

Sol.  $K_1 = \frac{\ln 2}{40}$

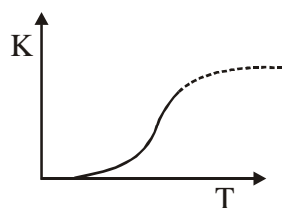
$$K_0 = \frac{1.386}{2 \times 20}$$

$$\frac{K_1}{K_0} = 0.5$$

14. Plots showing the variation of the rate constant (k) with temperature (T) are given below. The plot that follows Arrhenius equation is – [JEE 2010]



Ans. (A)



15. The concentration of R in the reaction  $R \rightarrow P$  was measured as a function of time and the following data is obtained :

| [R] (molar) | 1.0 | 0.75 | 0.40 | 0.10 |
|-------------|-----|------|------|------|
| t(min.)     | 0.0 | 0.05 | 0.12 | 0.18 |

The order of the reaction is.

[JEE 2010]

Ans. Zero

Sol. By hit and trial method the reaction is zero order.

$$K_1 = \frac{[A]_0 - [A]_1}{t_1}$$

$$K_1 = \frac{1 - 0.75}{0.05} = 5$$

$$K_2 = \frac{[A]_0 - [A]_2}{t_2}$$

$$K_2 = \frac{1 - 0.4}{0.12} = 5$$

As  $K_1 \approx K_2$  so reaction will be zero order reaction.

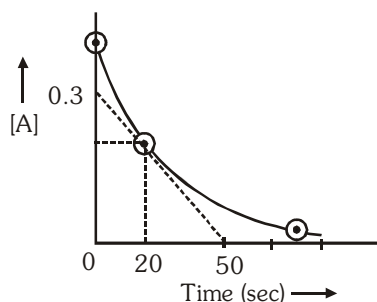


## EXERCISE # (S-1)

## RATE OF REACTION

- Ammonia and oxygen reacts at higher temperatures as  

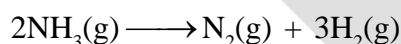
$$4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \longrightarrow 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$$
 In an experiment, the concentration of NO increases by  $1.08 \times 10^{-2} \text{ mol litre}^{-1}$  in 3 seconds. Calculate.  
 (i) rate of reaction  
 (ii) rate of disappearance of ammonia  
 (iii) rate of formation of water
- The reaction  $2\text{A} + \text{B} + \text{C} \rightarrow \text{D} + \text{E}$  is found to be first order in A, second order in B and zero order in C.  
 (i) Give the rate law for the reaction in the form of differential equation.  
 (ii) What is the effect in rate of increasing concentrations of A, B, and C two times?
- At  $27^\circ\text{C}$ , it was observed during a reaction of hydrogenation that the pressure of hydrogen gas decreases from 2 atmosphere to 1.1 atmosphere in 75 minutes. Calculate the rate of disappearance reaction in  $\text{M sec}^{-1}$  and in terms of  $\text{atm min}^{-1}$ . [Use :  $R = 0.08 \text{ atm-L/K-mole}$ ]
- For the elementary reaction  $2\text{A} + \text{B}_2 \longrightarrow 2\text{AB}$ . Calculate how much the rate of reaction will change if the volume of the vessel is suddenly reduced to one third of its original volume?
- For the reaction  $3\text{BrO}^- \rightarrow \text{BrO}_3^- + 2\text{Br}^-$  in an alkaline aqueous solution, the value of the second order (in  $\text{BrO}^-$ ) rate constant at  $80^\circ\text{C}$  in the rate law for  $-\frac{d[\text{BrO}^-]}{dt}$  was found to be  $0.057 \text{ L mol}^{-1} \text{ s}^{-1}$ . What is the rate constant when the rate law is written for :  
 (a)  $\frac{d[\text{BrO}_3^-]}{dt}$ , (b)  $\frac{d[\text{Br}^-]}{dt}$  ?
- $x\text{A} + y\text{B} \rightarrow z\text{C}$ . If  $-\frac{d[\text{A}]}{dt} = -\frac{d[\text{B}]}{dt} = 1.5 \frac{d[\text{C}]}{dt}$ , then  $(x + y + z)$  is. ( $x, y$  &  $z$  are the lowest integral value.)
- For the reaction :  $3\text{A}(\text{g}) \rightarrow 2\text{B}(\text{g})$ , the rate of formation of 'B' at  $298 \text{ K}$ , is represented as  $\ln \left( \frac{d[\text{B}]}{dt} \right) = -0.04 + 2 \times \ln[\text{A}]$ . The order of reaction is-
- A certain reaction  $\text{A} \rightarrow \text{B}$  follows the given concentration (Molarity) – time graph. Calculate the rate for this reaction at 20 second.



9. The reaction  $A(g) + 2B(g) \longrightarrow C(g) + D(g)$  is an elementary process. In an experiment, the initial partial pressure of A & B are  $P_A = 0.6$  and  $P_B = 0.8$  atm. Calculate the ratio of rate of reaction relative to initial rate when  $P_C$  becomes 0.2 atm.

### ZERO ORDER REACTIONS

10. In the reaction  $(A \longrightarrow B)$  rate constant is  $1.2 \times 10^{-2} \text{ M s}^{-1}$ . What is concentration of B after 10 and 20 min., if we start with 10 M of A.
11. From the following data for the zero order reaction :  $A \longrightarrow \text{products}$ . Calculate the value of k.
- | Time (min.) | [A]    |
|-------------|--------|
| 0.0         | 0.10 M |
| 1.0         | 0.09 M |
| 2.0         | 0.08 M |
12. A drop of solution (volume 0.10 ml) contains  $6 \times 10^{-6}$  mole of  $H^+$ . If the rate constant of disappearance of  $H^+$  is  $1 \times 10^7 \text{ mole litre}^{-1} \text{ sec}^{-1}$ , how long would it take for  $H^+$  in drop to disappear?
13. A certain substance A is mixed with an equimolar quantity of substance B. At the end of an hour A is 75% reacted. Calculate the time when A is 10% unreacted. (Given: order of reaction is zero for both A & B.)
14. For a zero order chemical reaction,

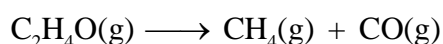


rate of reaction = 0.1 atm/sec. Initially only  $NH_3$  is present & its pressure = 3 atm. Calculate total pressure at  $t = 10$  sec.

### FIRST ORDER REACTIONS

15. A first order reaction is 75% completed in 72 min. How long time will it take for  
(i) 50% completion (ii) 87.5% completion
16. A first order reaction is 20% complete in 10 min. Calculate (i) the specific rate constant, (ii) the time taken for the reactions to go to 75% completion. [ $\ln 10 = 2.3$ ,  $\ln 2 = 0.7$ ]
17. Show that in case of unimolecular reaction, the time required for 99.9% of the reaction to take place is ten times that required for half of the reaction.
18. A drug is known to be ineffective after it has decomposed 75%. The original concentration of a sample was 500 units/ml. When analyzed 20 months later, the concentration was found to be 250 units/ml. Assuming that decomposition is of I order, what will be the expiry time of the drug?
19. A viral preparation was inactivated in a chemical bath. The inactivation process was found to be first order in virus concentration. At the beginning of the experiment, 2.0 % of the virus was found to be inactivated per minute. Evaluate k for inactivation process. [ $\ln 10 = 2.3$ ,  $\ln 98 = 4.58$ ]
20. The reaction  $SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$  is a first order gas reaction with  $k = \left(\frac{35}{9}\right) \times 10^{-4} \text{ sec}^{-1}$  at  $320^\circ\text{C}$ . What % of  $SO_2Cl_2$  is decomposed on heating this gas for 90 min. ( $\ln 2 = 0.7$ )
21. The decomposition of a compound A in solution follow first order kinetics. If 10% w/v solution of A is 10% decomposed in 10 minutes at  $10^\circ\text{C}$ , then 20% w/v solution of A is ..... % decomposed in 20 minutes at  $10^\circ\text{C}$ .

22. Calculate the half-life of the first-order reaction



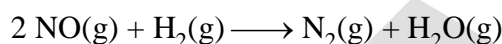
if the initial pressure of  $\text{C}_2\text{H}_4\text{O(g)}$  is 80 mm of Hg and the total pressure at the end of 20 minutes is 120 mm of Hg

### SECOND ORDER REACTIONS

23. In the II order reaction :  $2\text{A} \rightarrow \text{A}_2$ . The rate of formation of  $\text{A}_2$  is  $10^{-5} \text{ M sec}^{-1}$  at 0.01M concentration of A. Calculate the rate constant in the rate of disappearance of 'A'.
24. If  $t_{1/2}$  of a second order reaction is 1.0 hr. After what time, the amount of reactant will be 25% of the initial amount?
25. Reaction :  $\text{A} + \text{B} \rightarrow \text{C} + \text{D}$ , follows the rate law :  $r = (2 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}) [\text{A}] [\text{B}]$ . The reaction is started with 1.0 mole each of 'A' and 'B', in constant volume of 5 litre. In what time, the moles of 'A' become 0.25 ?

### DETERMINATION OF ORDER OF REACTION & RATE LAW

26. At  $800^\circ \text{C}$ , the rate of reaction



changes with the concentration of  $\text{NO(g)}$  and  $\text{H}_2\text{(g)}$  as-

| Exp.no. | [NO] in M            | [H <sub>2</sub> ] in M | $-\frac{1}{2} \frac{d[\text{NO}]}{dt}$ in $\text{M sec}^{-1}$ |
|---------|----------------------|------------------------|---------------------------------------------------------------|
| (i)     | $1.5 \times 10^{-3}$ | $4 \times 10^{-3}$     | $4.50 \times 10^{-9}$                                         |
| (ii)    | $1.5 \times 10^{-3}$ | $2 \times 10^{-3}$     | $2.25 \times 10^{-9}$                                         |
| (iii)   | $3.0 \times 10^{-3}$ | $2 \times 10^{-3}$     | $9.00 \times 10^{-9}$                                         |

- (a) What is the order of reaction?
- (b) What is the rate equation for the reaction?
- (c) What is the rate of reaction when  $[\text{H}_2] = 1.5 \times 10^{-3} \text{ M}$  and  $[\text{NO}] = 1.0 \times 10^{-3} \text{ M}$ ?
27. The catalytic decomposition of  $\text{N}_2\text{O(g)}$  by gold at  $900^\circ \text{C}$  and at an initial pressure of 200 mm is 50% complete in 53 minutes and 73% complete in 100 minutes.
- (i) What is the order of the reaction?
- (ii) Calculate the velocity constant.
- (iii) How much of percentage  $\text{N}_2\text{O(g)}$  will decompose in 100 min. at the same temperature but at initial pressure of 600 mm of Hg ?
28. The pressure of a gas decomposing at the surface of a solid catalyst has been measured at different time and the results are given below

| t (sec)      | 0               | 100               | 200             | 300               |
|--------------|-----------------|-------------------|-----------------|-------------------|
| Pr. (Pascal) | $4 \times 10^3$ | $3.5 \times 10^3$ | $3 \times 10^3$ | $2.5 \times 10^3$ |

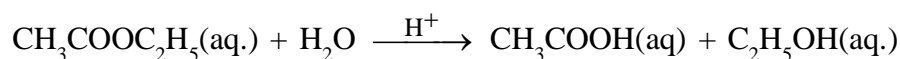
Determine the order of reaction and its rate constant.

29. The half life period of decomposition of a compound is 50 minutes. If the initial concentration is halved, the half life period is reduced to 25 minutes. What is the order of reaction?
30. For a chemical reaction  $\text{A} + \text{B} \rightarrow \text{products}$ , the order is one with respect to each A and B. The sum of x and y from the following data is.

| Rate ( $\text{mol l}^{-1} \text{s}^{-1}$ ) | [A] ( $\text{mol l}^{-1}$ ) | [B] ( $\text{mol l}^{-1}$ ) |
|--------------------------------------------|-----------------------------|-----------------------------|
| 0.10                                       | 0.20                        | 0.05                        |
| 0.40                                       | x                           | 0.05                        |
| 0.80                                       | 0.40                        | y                           |



39. For the hydrolysis of ethyl acetate in presence of  $H^+$  as catalyst.



the experimentally observed rate law is

$$\text{rate} = k [\text{ester}] [H_2O] [H^+].$$

If the value of rate constant is  $1.386 \times 10^{-3} M^{-2} \text{min}^{-1}$  and concentration of  $[H^+]$  ion is 1.8 M, how many seconds will it take for concentration of ester to become half of initial value ?

40. If 0.01 % of a substance undergoing decomposition is consumed in 1 milli seconds when the concentration is 0.02M and in 0.25 milli seconds when the concentration is 0.04M. The order of reaction is.

### PARALLEL , SEQUENTIAL REACTIONS AND REVERSIBLE

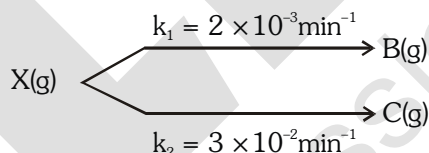
41.  $A \begin{cases} \xrightarrow{k_1} B \\ \xrightarrow{k_2} C \end{cases}$ ,  $k_1 = x \text{ hr}^{-1}$ ;  $k_1 : k_2 = 1 : 10$ . Calculate  $\frac{[C]}{[A]}$  after one hour from the start of the reaction.

Assuming only A was present in the beginning.

42. How much time would be required for the B to reach maximum concentration for the reaction



43. A gaseous reactant X decompose to produce gaseous product B & C in a parallel reaction, both by first order, as follows :



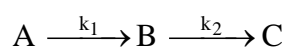
If the decomposition is carried out in a sealed flask, partial pressure of B after very long time was found to be 100 mm Hg. Determine the time when pressure of X(g) was 100 mm Hg.

$$[\ln 2 = 0.693]$$

44. The reaction A proceeds in parallel channels  $A \begin{cases} \rightarrow B \\ \rightarrow C \end{cases}$ . Suppose the half life values for the two branches

are 60 minutes and 90 minutes, what is the overall half-life value?

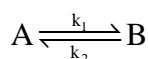
45. For the given sequential reaction



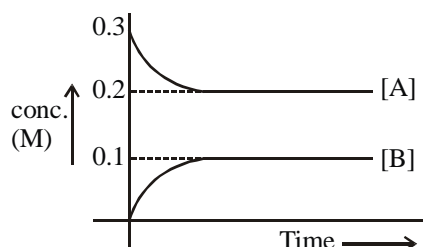
Initial concentration of A is 20M. Calculate the approximate concentration of C after 10 min,

$$\text{if } k_1 = 2 \times 10^8 \text{ min}^{-1} \text{ \& } k_2 = 0.0693 \text{ min}^{-1}$$

46. Consider a reversible reaction :



Which is a first order in both the direction ( $k_1 = \frac{1.38}{3} \times 10^{-2} \text{ min}^{-1}$ ). The variation in concentration is plotted with time as shown below.



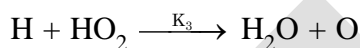
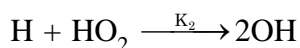
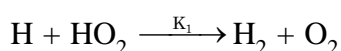
Calculate the time (in minute) at which 25% of A would be exhausted. [ $\ln 2 = 0.69$ ]

47. 3 mole mixture of two different substances A & B (mole fraction of A = 2/3) undergoes parallel first order reaction to form product 'C' as follow at 300 K.



The time at which there will be 2 mole of 'C' is

48. For the series of competitive reactions :



It has been found that  $K_1 : K_2 : K_3 = 0.60 : 0.30 : 0.10$ . The molar ratio of the product,  $H_2$ ,  $O_2$ ,  $OH$ ,  $H_2O$  and  $O$ , at time  $t$ , is -

49. In the parallel reactions :  $A \xrightarrow{K_1 = \ln 3 \text{ min}^{-1}} B$  and  $A \xrightarrow{K_2 = \ln 3 \text{ min}^{-1}} C$ , the time when the concentration of A, B and C becomes equal is -

50. For the sequential reactions :

$A \xrightarrow{K_1 = 0.02 \text{ min}^{-1}} B \xrightarrow{K_2 = 0.02 \text{ min}^{-1}} C$ , the initial concentration of 'A' was 0.2M and initially 'B' and 'C' were absent. The time at which the concentration of 'B' becomes maximum and the maximum concentration of 'B' are respectively.

### TEMPERATURE DEPENDENCE OF RATE

51. In gaseous reactions important for understanding the upper atmosphere,  $H_2O$  and  $O$  react bimolecularly to form two  $OH$  radicals.  $\Delta H$  for this reaction is 72 kJ at 500 K and  $E_a = 77 \text{ kJ mol}^{-1}$ , then calculate  $E_a$  for the bimolecular recombination of  $2OH$  radicals to form  $H_2O$  &  $O$  at 500 K
52. The specific rate constant for a reaction increases by a factor of 4, if the temperature is changed from  $27^\circ\text{C}$  to  $47^\circ\text{C}$ . Find the activation energy (in kcal) for the reaction (Use  $\ln 2 = 0.7$ )
53. Given that the temperature coefficient for the saponification of ethyl acetate by  $NaOH$  is 1.75. Calculate activation energy for the saponification of ethyl acetate. Let initial temperature is 298K.

[Use :  $\ln (1.75) = 0.56$ ]

54. The energy of activation for a reaction is at 27°C 10 kJ/mol. The presence of catalyst lowers the energy of activation by 75%. Find the factor by which rate of reaction increases at 27°C due to catalyst. (Take  $R = 25/3 \text{ J/mol-k}$ )

55. At 380°C, the half-life period for the first order decomposition of  $\text{H}_2\text{O}_2$  is 360 min. The energy of activation of the reaction is 200 kJ mol<sup>-1</sup>. Calculate the time required for 75% decomposition at 450°C.

Use :  $\left[ \frac{1}{653} - \frac{1}{723} \right] = 1.5 \times 10^{-4}$ ,  $e^{3.6} = 36$ ,  $R = \frac{25}{3} \text{ J/k-mol}$

56. The rate constant for decomposition of  $\text{COCl}_2$  (g) according to following reaction  $\text{COCl}_2(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{Cl}_2(\text{g})$ ;  $\Delta H = 19 \text{ kcal/mol}$ , is expressed as

$$\ln k = 15 - \frac{5000}{T}$$

Calculate activation energy for given reaction (in Kcal/mol.)

57. At 300 K, 50% of molecule collide with energy greater than or equal to  $E_a$ . At what temperature, 25% molecule will have energy greater than or equal to  $E_a$ .

58. For a zero order reaction at 200K reaction complete in 5 minutes while at 300K, same reaction completes in 2.5 minutes. What will be the activation energy in calorie.

( $R = 2 \text{ Cal/mol-k}$ ;  $\ln 2 = 0.7$ )

59. For a first order reaction :  $A \rightarrow P$ , the temperature (T) dependent rate constant (k) was found to follow the equation  $\log_{10} k = -(2000) \frac{1}{T} + 6$ . Then activation energy equation of reaction will be ( $\ln x = 2.3 \times \log x$ )

60. A reaction takes place in three steps. The rate constants are  $k_1$ ,  $k_2$ ,  $k_3$ . The overall rate constant  $k = \frac{k_1 \sqrt{k_3}}{k_2}$ . If energy of activation is 40, 30 and 20 kJ respectively, the overall energy of activation is :

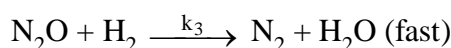
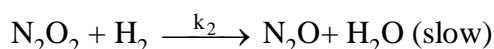
### MECHANISM OF REACTION

61. The reaction  $2\text{NO} + \text{Br}_2 \longrightarrow 2\text{NOBr}$ , is supposed to follow the following mechanism



Suggest the rate law expression.

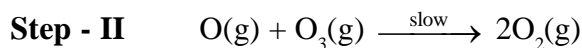
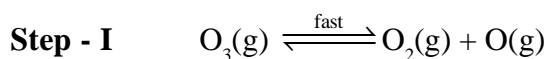
62. For the reaction  $2\text{H}_2 + 2\text{NO} \longrightarrow \text{N}_2 + 2\text{H}_2\text{O}$ , the following mechanism has been suggested :



Establish the rate law for given reaction.

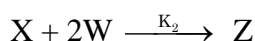
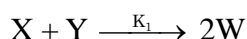
63. For the reaction :  $2\text{O}_3(\text{g}) \longrightarrow 3\text{O}_2(\text{g})$

**Mechanism :**



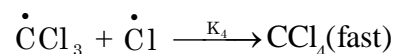
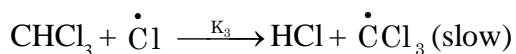
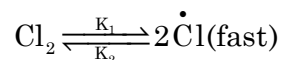
Overall order of reaction based on mechanism is

64. A complex reaction :  $2\text{X} + \text{Y} \rightarrow \text{Z}$ , takes place in two steps :



If  $\text{K}_1 \ll \text{K}_2$ , order of reaction will be -

65. The suggested mechanism for the reaction :  $\text{CHCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow \text{CCl}_4(\text{g}) + \text{HCl}(\text{g})$ , is -



The experimental rate law consistent with the mechanism.



## EXERCISE # (S-2)

- The decomposition of a compound P, at temperature T according to the equation  

$$2P_{(g)} \longrightarrow 4Q_{(g)} + R_{(g)} + S_{(l)}$$
is the first order reaction. After 30 minutes from the start of decomposition in a closed vessel, the total pressure developed is found to be 317 mm Hg and after a long period of time the total pressure observed to be 617 mm Hg. Calculate the total pressure of the vessel after 75 minutes, if volume of liquid S is supposed to be negligible. Also calculate the time fraction  $t_{7/8}$ .  
**Given :** Vapour pressure of S (l) at temperature T = 32.5 mm Hg.  
 $[\ln = 1.169] = 0.156, \ln 2 = 0.7, e^{0.39} = 1.5]$
- For the reaction :  $A + B \longrightarrow \text{Product}$ , rate law is :  $\text{rate} = k [A]^2 [B]$ , where  $k = 5 \times 10^{-5} (\text{mol/L})^{-2} \text{min}^{-1}$ . Determine the **time (in minutes)** in which concentration of 'A' becomes half of its initial concentration, if initial concentration of A and B are 0.2 M and  $2 \times 10^3$  M respectively.
- An optically active compound A upon acid catalysed hydrolysis yield two optically active compound B and C by pseudo first order kinetics. The observed rotation of the mixture after 20 min was  $5^\circ$  while after completion of the reaction it was  $-20^\circ$ . If optical rotation per mole of A, B & C are  $60^\circ$ ,  $40^\circ$  &  $-80^\circ$ . Calculate half life of the reaction.
- The reaction  

$$\text{cis-Cr(en)}_2(\text{OH})_2^+ \xrightleftharpoons[k_2]{k_1} \text{trans-Cr(en)}_2(\text{OH})_2^+$$
is first order in both directions. At  $25^\circ\text{C}$ , the equilibrium constant is 0.1 and the rate constant  $k_1$  is  $2 \times 10^{-4} \text{s}^{-1}$ . In an experiment starting with the pure *cis* form, how long would it take for half the equilibrium amount of the *trans* isomer to be formed ?  $[\ln 2 = 0.693]$
- For the two parallel first order reactions  $A \xrightarrow{k_1} B$  and  $A \xrightarrow{k_2} C$ , show that the activation energy  $E'$  for the disappearance of A is given in terms of activation energies  $E_1$  and  $E_2$  for the two paths by  

$$E' = \frac{k_1 E_1 + k_2 E_2}{k_1 + k_2}$$
- At room temperature ( $27^\circ\text{C}$ ), orange juice gets spoilt in about 64 hours. In a refrigerator at  $7^\circ\text{C}$ , juice can be stored three times as long before it gets spoilt. Estimate  
(a) the activation energy of the reaction that causes the spoiling of juice.  
(b) How long should it take for juice to get spoilt at  $47^\circ\text{C}$ ?  
 $[e^{0.9625} = 2.5, \ln 3 = 1.1, R = 2 \text{ cal/mol-K}]$
- Two reactions (i)  $A \rightarrow \text{products}$  (ii)  $B \rightarrow \text{products}$ , follow first order kinetics. The rate of the reaction (i) is doubled when the temperature is raised from 300 K to 310K. The half life for this reaction at 310K is 30 minutes. At 310K temperature and same concentration of reactant in both reactions B, decomposes twice as fast as A. If the energy of activation for the reaction (ii) is half that of reaction (i), calculate the rate constant of the reaction (ii) at 300K.

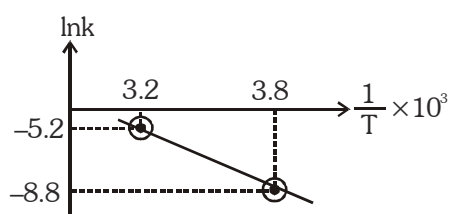
- 8.** The reaction of formation of phosgene from CO and Cl<sub>2</sub> is  $\text{CO} + \text{Cl}_2 \longrightarrow \text{COCl}_2$   
The proposed mechanism is



Show that the above mechanism leads to the following rate law  $\frac{d[\text{COCl}_2]}{dt} = k[\text{CO}][\text{Cl}_2]^{3/2}$ ,

$$\text{where } K = k_3 \cdot \frac{k_2}{k_{-2}} \left( \frac{k_1}{k_{-1}} \right)^{1/2}.$$

- 9.** For any elementary reaction, following observation is made :



If the above reaction is carried out in the presence of catalyst at 300K, the reaction proceeds with same rate as without catalyst at 400K. By what amount (in kcal) catalyst has decreased  $E_a$ .

10. Milk is pasteurised if it is heated at  $67^{\circ}\text{C}$  for 4 hours. If  $\frac{E_a}{2.303}$  for the process is  $23.8 \text{ kcal/mol}$  then minimum how much seconds will be required for the the process at  $77^{\circ}\text{C}$  ? [ $R = 2 \text{ cal/K-mol}$ ]
11. When  $\text{CrI}_3$  reacts with  $\text{H}_2\text{O}_2$  in presence of  $\text{NaOH}$  forming  $\text{Na}_2\text{CrO}_4$ ,  $\text{NaIO}_4$  &  $\text{H}_2\text{O}$  then find how many times will be rate of disappearance of  $\text{NaOH}$  compared to  $\text{CrI}_3$ .
12. Conversion of A into B and C follows first order kinetics. A, B and C all are optically active, initially A is present in 500 ml solution and 100 minutes after the start of reaction, the resulting solution becomes optically inactive. If angle of rotation of A is  $+50$  degree per molar, B is  $-20$  degree per molar and C is  $+10$  degree per molar, then find the time for completion of  $\left(\frac{875}{9}\right)\%$  of the chemical reaction in minutes.



13. A gas phase reaction is,  

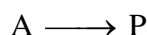
$$\text{A(g)} + 2\text{B(g)} \rightarrow \text{C(g)}$$

The reaction was carried out with stoichiometric proportions of A and B and the following data is obtained

|                                   |               |               |
|-----------------------------------|---------------|---------------|
| <b>Half life (min)</b>            | <b>10</b>     | <b>160</b>    |
| <b>Initial pressure of A(atm)</b> | <b>40 atm</b> | <b>10 atm</b> |

What is overall order of reaction

14. For the reaction



If ratio of  $t_{7/8} : t_{1/4}$  is 7 : 2 what is order of reaction.

$t_{7/8}$  = time in which 7/8 part of reactant is reacted

$t_{1/4}$  = time in which 1/4 part of reactant is reacted

15. A certain reactant  $A^{n+}$  is getting converted to  $A^{(n+4)+}$  in solution. The rate constant of this reaction is measured by titrating a volume of the solution with a reducing reagent which only reacts with  $A^{n+}$  and  $A^{(n+4)+}$ . In this process, it converts  $A^{n+}$  to  $A^{(n-2)+}$  and  $A^{(n+4)+}$  to  $A^{(n-1)+}$ .

**Time** 0 10 min

**Volume of** 30 ml 45 ml

**reagent consumed**

Calculate the rate constant (in  $\text{min}^{-1}$ ) of the conversion of  $A^{n+}$  to  $A^{(n+4)+}$  assuming it to be first order reaction.

[n-factor of reagent remain same when it reacts with  $A^{n+}$  &  $A^{(n+4)+}$ ]

[Given:  $\ln 3/2 = 0.4$ ]

16. Consider two 1<sup>st</sup> order reactions at 25°C with same initial concentrations of 1M

I.  $A \xrightarrow{t_{1/2} = 40 \text{ min}}$  product (temperature coefficient = 2)

II.  $B \xrightarrow{t_{1/2} = 30 \text{ min}}$  product (temperature coefficient = 3)

If both reactions are carried out at 35°C. Find ratio of concentrations of A & B after one hour.

17. Consider two reactions at 27°C

(I).  $A \longrightarrow B$  ; ( First order kinetics)

(II).  $X \longrightarrow Y$  ; ( Zero order kinetics)

If both A & X each having initial concentration 0.1M & same half life period. Then find simplest ratio of rate constants for I & II reactions. [ $\ln 2 = 0.7$ ]

18. The rate of first-order reaction is  $0.04 \text{ mol litre}^{-1} \text{ s}^{-1}$  at 10 minutes and  $0.03 \text{ mol litre}^{-1} \text{ s}^{-1}$  at 22 minutes after initiation. The half life of the reaction (in seconds) is ( $\ln 2 = 0.7$ ,  $\ln 3 = 1.1$ ).

19. In order to determine the order of reaction :  $A(g) \rightarrow 2B(g)$ , vapour density of the system is determined at different stages of reaction, at constant temperature. The reaction is started with pure A(g). From the following data, the order of reaction is -

**Time (min)** 0 10 20

**Vapour density** 42 35 30

20. In the reaction :  $A \rightarrow P$ , the rate is doubled when the concentration of 'A' is quadrupled. If 50% of the reaction occurs in  $8\sqrt{2}$  hr, how long (in hours) would it take for the completion of next 50% reaction.

# EXERCISE # (O-1)

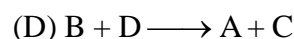
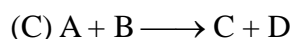
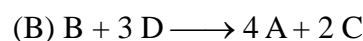
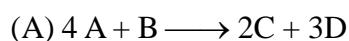
## SINGLE CORRECT

### RATE OF REACTION

1. The rate of a reaction is expressed in different ways as follows :

$$+\frac{1}{2} \frac{d[C]}{dt} = -\frac{1}{3} \frac{d[D]}{dt} = +\frac{1}{4} \frac{d[A]}{dt} = -\frac{d[B]}{dt}$$

The reaction is:



2. For the reaction  $2A + 3B \rightarrow 4C$   
the rate of reaction may be represented as :-

(A)  $r = -2 \frac{d(A)}{dt} = -3 \frac{d(B)}{dt} = 4 \frac{d(C)}{dt}$

(B)  $r = -2 \frac{d(A)}{dt} = -4 \frac{d(B)}{dt} = 3 \frac{d(C)}{dt}$

(C)  $r = -\frac{1}{2} \frac{d(A)}{dt} = \frac{1}{3} \frac{d(B)}{dt} = \frac{1}{4} \frac{d(C)}{dt}$

(D)  $r = -\frac{1}{2} \frac{d(A)}{dt} = -\frac{1}{3} \frac{d(B)}{dt} = \frac{1}{4} \frac{d(C)}{dt}$

3. In a reaction  $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$ , the rate of appearance of  $NH_3$  is  $2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ sec}^{-1}$ . The rate of reaction & rate of disappearance of  $H_2$  will be (In  $\text{mol L}^{-1} \text{ sec}^{-1}$ )

(A)  $3.75 \times 10^{-4}, 1.25 \times 10^{-4}$

(B)  $1.25 \times 10^{-4}, 2.5 \times 10^{-4}$

(C)  $1.25 \times 10^{-4}, 3.75 \times 10^{-4}$

(D)  $5.0 \times 10^{-4}, 3.75 \times 10^{-4}$

4. For the reaction  $4A + B \rightarrow 2C + 2D$ , the incorrect statement is :-

(A) The rate of disappearance of B is one fourth the rate of disappearance of A

(B) The rate of appearance of C is half the rate of disappearance of B

(C) The rate of formation of D is half the rate of consumption of A

(D) The rates of formation of C and D are equal

5. Which of the following rate law has an overall order of 0.5 for reaction involving substances x,y and z ?

(A) Rate =  $k [C_x] [C_y] [C_z]$

(B) Rate =  $k [C_x]^{0.5} [C_y]^{0.5} [C_z]^{0.5}$

(C) Rate =  $k [C_x]^{1.5} [C_y]^{-1} [C_z]^0$

(D) Rate =  $k [C_x] [C_z]^0 / [C_y]^2$

6. For a reaction  $A + B \rightarrow \text{products}$ , the rate of the reaction was doubled when the concentration of A was doubled, the rate was again doubled when the conc. of A & B were doubled. The order of the reaction with respect to A & B are:-

(A) 1, 1

(B) 2, 0

(C) 1, 0

(D) 0, 1

7. If the rate of the reaction is equal to the rate constant, the order of the reaction is:-

(A) 0

(B) 1

(C) 2

(D) 3

8. If the first order reaction involves gaseous reactants and gaseous products the units of its rate may be -

(A) atm.

(B) atm - sec.

(C) atm -  $\text{sec}^{-1}$

(D)  $\text{atm}^2 \text{ sec}^2$

9. If concentration of reactants is increased by 'x', then the rate constant (k) becomes :-

(A)  $\ln \frac{k}{x}$

(B)  $\frac{k}{x}$

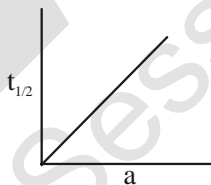
(C)  $k + x$

(D) k

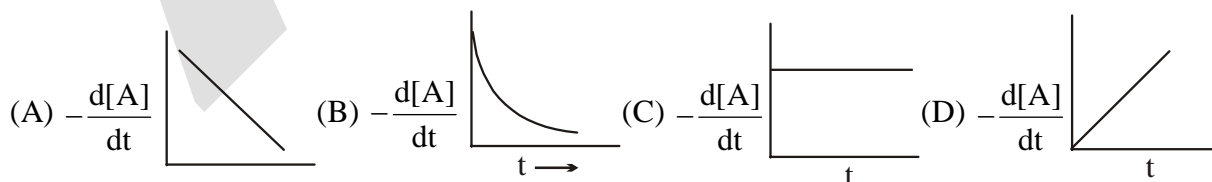
10. The rate constant of  $n^{\text{th}}$  order reaction has units  
 (A)  $\text{litre}^{1-n} \text{ mol}^{1-n} \text{ sec}^{-1}$  (B)  $\text{mol}^{n-1} \text{ litre}^{1-n} \text{ sec}^{-1}$   
 (C)  $\text{mol}^{1-n} \text{ litre}^{n-1} \text{ sec}^{-1}$  (D) None
11. A reaction is found to have the rate constant  $x \text{ sec}^{-1}$ . By what factor the rate is increased if initial conc. of A is tripled ?  
 (A) 3 (B) 9 (C)  $x$  (D) Remains same
12. Consider following two reactions  
 $A \longrightarrow \text{Product} ; -\frac{d[A]}{dt} = k_1 [A]^0$   
 $B \longrightarrow \text{Product} ; -\frac{d[B]}{dt} = k_2 [B]$   
 $k_1$  and  $k_2$  are expressed in terms of molarity ( $\text{mol L}^{-1}$ ) and time (sec) as  
 (A)  $\text{sec}^{-1}$ ,  $\text{M sec}^{-1}$  (B)  $\text{M sec}^{-1}$ ,  $\text{M sec}^{-1}$  (C)  $\text{sec}^{-1}$ ,  $\text{M}^{-1} \text{ sec}^{-1}$  (D)  $\text{M sec}^{-1}$ ,  $\text{sec}^{-1}$
13.  $A(g) \longrightarrow B(g) + 3C(g)$   
 In a closed container at a given temperature, pressure increases from 100 mm Hg to 160 mm Hg in 10 sec. for reaction.  
 Then the average rate of reaction in first 10 sec. will be -  
 (A) 2 mm/sec. (B) 4 mm/sec. (C) 6 mm/sec. (D) 3 mm/sec.

### ZERO ORDER REACTION

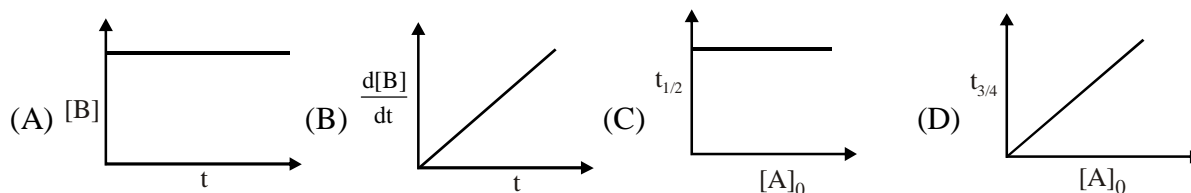
14.  $H_2$  gas is adsorbed on the metal surface like tungsten. This follows ..... order reaction -  
 (A) Third (B) Second (C) Zero (D) First
15. The rate constant of a zero order reaction is  $0.2 \text{ mol dm}^{-3} \text{ h}^{-1}$ . If the concentration of the reactant after 30 minutes is  $0.05 \text{ mol dm}^{-3}$ . Then its initial concentration would be :  
 (A)  $0.15 \text{ mol dm}^{-3}$  (B)  $1.05 \text{ mol dm}^{-3}$  (C)  $0.25 \text{ mol dm}^{-3}$  (D)  $4.00 \text{ mol dm}^{-3}$
16. Consider the reaction  $A \longrightarrow B$ , graph between half life ( $t_{1/2}$ ) and initial concentration (a) of the reactant is



Hence graph between  $-\frac{d[A]}{dt}$  and time will be



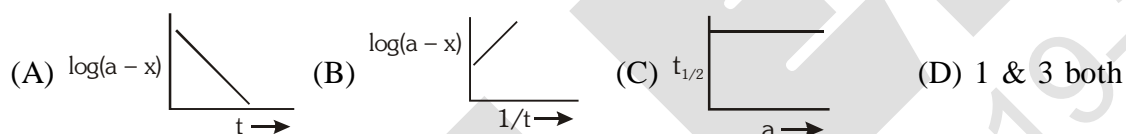
17. Which graph represents zero order reaction  $[A(g) \rightarrow B(g)]$  :



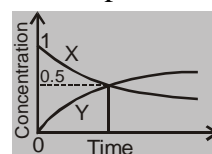
18.  $k$  for a zero order reaction is  $2 \times 10^{-2} \text{ mol L}^{-1} \text{ sec}^{-1}$ . If the concentration of the reactant after 25 sec is 0.5 M, then concentration after 50 sec. must have been.  
 (A) 0.5 M (B) 0.25 M (C) 0.125 M (D) 0.0 M

**FIRST ORDER REACTION**

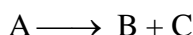
19. The rate constant of a first order reaction is  $4 \times 10^{-3} \text{ sec}^{-1}$ . At a reactant concentration of 0.02 M, the rate of reaction would be –  
 (A)  $8 \times 10^{-5} \text{ M sec}^{-1}$  (B)  $4 \times 10^{-3} \text{ M sec}^{-1}$   
 (C)  $2 \times 10^{-1} \text{ M sec}^{-1}$  (D)  $4 \times 10^{-1} \text{ M sec}^{-1}$
20. In a first order reaction the concentration of the reactant is decreased from 1.0 M to 0.25 M in 20 min. The rate constant of the reaction would be –  
 (A)  $10 \text{ min}^{-1}$  (B)  $6.931 \text{ min}^{-1}$  (C)  $0.6931 \text{ min}^{-1}$  (D)  $0.06931 \text{ min}^{-1}$
21. A first order reaction has a half life period of 69.3 sec. At 0.10 mol  $\text{lit}^{-1}$  reactant concentration rate will be –  
 (A)  $10^{-4} \text{ M sec}^{-1}$  (B)  $10^{-3} \text{ M sec}^{-1}$  (C)  $10^{-1} \text{ M sec}^{-1}$  (D)  $6.93 \times 10^{-1} \text{ M sec}^{-1}$
22. What fraction of a reactant (in first order reaction) is left after 40 minute if  $t_{1/2}$  is 20 minute  
 (A) 1/4 (B) 1/2 (C) 1/8 (D) 1/6
23. Which of the following curve represents a 1<sup>st</sup> order reaction :–



24. After how many seconds will the conc. of the reactant in a first order reaction be halved, if the rate constant is  $1.155 \times 10^{-3} \text{ sec}^{-1}$  :-  
 (A) 600 (B) 100 (C) 60 (D) 10
25. Correct statement about first order reaction is:-  
 (A)  $t_{\text{completion}} = \text{finite}$  (B)  $t_{1/2} \propto \frac{1}{a}$   
 (C) Unit of  $k$  is  $\text{mole lit}^{-1} \text{ sec}^{-1}$  (D)  $t_{1/2} \times k = \text{const.}$
26. For a given reaction of first order, it takes 20 minute for the concentration to drop from 1 M to 0.6 M. The time required for the concentration to drop from 0.6 M to 0.36 M will be :  
 (A) More than 20 min (B) Less than 20 min  
 (C) Equal to 20 min (D) Infinity
27. The accompanying figure depicts the change in concentration of species X and Y for the reaction  $X \rightarrow Y$  as a function of time. The point of intersection of the two curves represents.  
 (A)  $t_{1/2}$   
 (B)  $t_{3/4}$   
 (C)  $t_{2/3}$   
 (D) Data insufficient to predict
28. A reaction is of first order. After 100 minutes, 75 g of the reactant A are decomposed when 100g are taken initially. Calculate the time required when 150g of the reactant A are decomposed, the initial weight taken is 200g.  
 (A) 100 minutes (B) 200 minutes (C) 150 minutes (D) 175 minutes



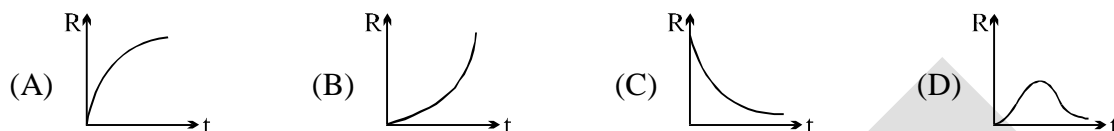
29. Consider the reaction :



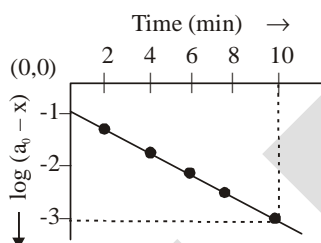
Initial concentration of A is 1 M. 20 minutes time is required for completion of 80 % reaction.

If  $\frac{d[B]}{dt} = k[A]$ , then half life ( $t_{1/2}$ ) is (Use :  $\ln 5 = 1.6$ ,  $\ln 2 = 0.7$ )

- (A) 55.44 min. (B) 50 min (C) 8.75 min (D) 12.5 min
30. If decomposition reaction  $A(g) \longrightarrow B(g)$  follows first order kinetics, then the graph of rate of formation (R) of B against time t will be



31. For the first order decomposition of  $SO_2Cl_2(g)$ ,  
 $SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$   
 a graph of  $\log(a_0 - x)$  vs t is shown in figure. What is the rate constant ( $\text{sec}^{-1}$ )?



- (A) 0.2 (B)  $4.6 \times 10^{-1}$  (C)  $7.7 \times 10^{-3}$  (D)  $1.15 \times 10^{-2}$
32. The rate constant for a second order reaction is  $8 \times 10^{-5} \text{ M}^{-1} \text{ min}^{-1}$ . How long will it take a 1M solution to be reduced to 0.5 M ?  
 (A)  $8.665 \times 10^3 \text{ min}$  (B)  $8 \times 10^{-3} \text{ min}$  (C)  $1.25 \times 10^4 \text{ min}$  (D)  $4 \times 10^{-5} \text{ min}$
33. The rate law of the reaction :  $A + 2B \rightarrow \text{product(P)}$  is given by  $\frac{d[P]}{dt} = K[A]^2[B]$ . If A is taken in large excess, the order of the reaction will be –  
 (A) Zero (B) 1 (C) 2 (D) 3

### CALCULATION OF ORDER OF REACTION

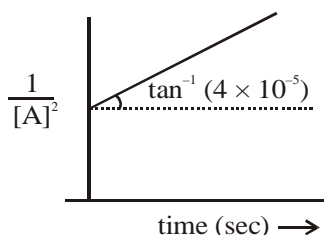
34. Time required to complete a half fraction of a reaction varies inversely to the concentration of reactant then the order of reaction is –  
 (A) Zero (B) 1 (C) 2 (D) 3
35. The reaction  $L \rightarrow M$  is started with 10 g of L. After 30 and 90 minute, 5 g and 1.25 g of L are left respectively. The order of reaction is –  
 (A) 0 (B) 2 (C) 1 (D) 3
36. From different sets of data of  $t_{1/2}$  at different initial concentrations say 'a' for a given reaction,  $[t_{1/2} \propto a]$  is found. The order of reaction is :–  
 (A) 0 (B) 1 (C) 2 (D) 3
37. At certain temperature, the half life period for the thermal decomposition of a gaseous substance depends on the initial partial pressure of the substance as follows

|                     |     |     |
|---------------------|-----|-----|
| P(mmHg)             | 500 | 250 |
| $t_{1/2}$ (in min.) | 235 | 950 |

Find the order of reaction [Given  $\log(23.5) = 1.37$  ;  $\log(95) = 1.97$ ;  $\log 2 = 0.30$ ]

- (A) 1 (B) 2 (C) 2.5 (D) 3

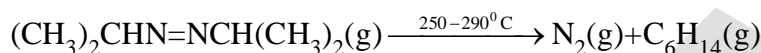
38. For a reaction  $A \longrightarrow \text{Product}$



What is the value of  $k$  for the given reaction-

- (A)  $4 \times 10^{-5} \text{ M}^{-1}\text{s}^{-1}$  (B)  $\frac{4}{3} \times 10^{-5} \text{ M}^{-2}\text{s}^{-1}$  (C)  $2 \times 10^{-5} \text{ M}^{-2}\text{s}^{-1}$  (D)  $\frac{2}{3} \times 10^{-5} \text{ M}^{-2}\text{s}^{-1}$

39. Azo isopropane decomposes according to the equation :-



It is found to be a first order reaction. If initial pressure is  $P_0$  and pressure of the mixture at time  $t$  is ( $P_t$ ) then rate constant  $K$  would be :-

- (A)  $k = \frac{2.303}{t} \log \frac{P_0}{2P_0 - P_t}$  (B)  $k = \frac{2.303}{t} \log \frac{P_0 - P_t}{P_0}$   
(C)  $k = \frac{2.303}{t} \log \frac{P_0}{P_0 - P_t}$  (D)  $k = \frac{2.303}{t} \log \frac{2P_0}{2P_0 - P_t}$

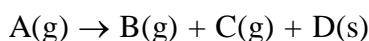
40. For a 1<sup>st</sup> order homogeneous gaseous reaction



if the pressure after time  $t$  was  $P_t$  and after long time was  $P_\infty$ , then rate constant ( $k$ ) in terms of  $P_t$  &  $P_\infty$  and  $t$  is -

- (A)  $k = \frac{2.303}{t} \log \left( \frac{P_\infty}{P_\infty - P_t} \right)$  (B)  $k = \frac{2.303}{t} \log \left( \frac{2P_\infty}{P_\infty - P_t} \right)$   
(C)  $k = \frac{2.303}{t} \log \left( \frac{2P_\infty}{3(P_\infty - P_t)} \right)$  (D) None of these

41. The first order reaction



taking place at constant pressure and temperature condition. Initially volume of the container containing only  $A$  was found to be  $V_0$  and after time ' $t$ ' it was  $V_t$ . Rate constant for the reaction is.

- (A)  $\frac{1}{t} \ln \frac{V_0}{2V_0 - V_t}$  (B)  $\frac{1}{t} \ln \frac{V_0}{V_0 - V_t}$  (C)  $\frac{1}{t} \ln \frac{2V_0}{2V_0 - V_t}$  (D)  $\frac{1}{t} \ln \frac{2V_0}{V_0 + V_t}$



42. For the inversion of cane sugar ( $C_{12}H_{22}O_{11}$ ) obeying I order following data were obtained

| Time (min.)                            | 0   | 10   | $\infty$ |
|----------------------------------------|-----|------|----------|
| Angle of rotation of solution (degree) | +20 | -2.5 | -10      |

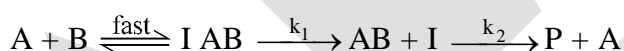
What will be rate constant in  $\text{min}^{-1}$  ( $\ln 2 = 0.7$ )

- (A) 0.7 (B) 0.14 (C) 0.21 (D) 0.07

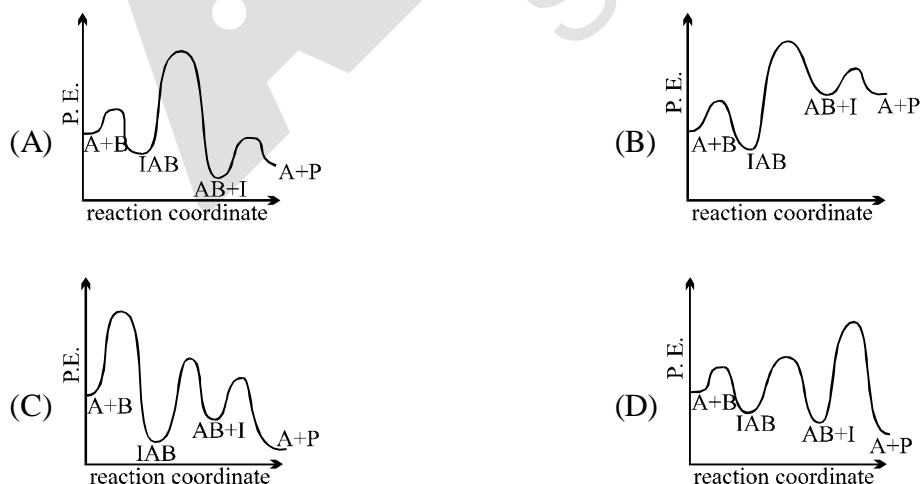
### COLLISION THEORY AND ARRHENIUS EQUATION

43. The rate constant for the forward reaction  $A(g) \rightleftharpoons 2B(g)$  is  $1.5 \times 10^{-3} \text{ s}^{-1}$  at 100 K. If  $10^{-5}$  moles of A and 100 moles of B are present in a 10 litre vessel at equilibrium then rate constant for the backward reaction at this temperature is  
 (A)  $1.50 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$  (B)  $1.5 \times 10^{11} \text{ L mol}^{-1} \text{ s}^{-1}$   
 (C)  $1.5 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$  (D)  $1.5 \times 10^{-11} \text{ L mol}^{-1} \text{ s}^{-1}$
44. According to collision theory of reaction –  
 (A) Every collision between reactant leads to chemical reaction  
 (B) Rate of reaction is proportional to velocity of molecules  
 (C) All reactions which occur in gaseous phase are zero order reaction  
 (D) Rate of reaction is directly proportional to collision frequency.
45. Activation energy of a reaction is –  
 (A) The energy released during the reaction  
 (B) The energy evolved when activated complex is formed  
 (C) Minimum amount of energy needed to overcome the potential barrier of reaction  
 (D) The energy needed to form one mole of the product
46. The minimum energy for molecules to enter into chemical reaction is called  
 (A) Kinetic energy (B) Potential energy (C) Threshold energy (D) Activation energy
47. For producing the effective collisions, the colliding molecules must possess:-  
 (A) A certain minimum amount of energy  
 (B) Energy equal to or greater than threshold energy  
 (C) Proper orientation  
 (D) Threshold energy as well as proper orientation of collision
48. A large increase in the rate of a reaction for a rise in temperature is due to –  
 (A) Increase in the number of collisions (B) Increase in the number of activated molecules  
 (C) Lowering of activation energy (D) Shortening of the mean free path
49. Slope of which plot can give the value of activation energy  
 (A) k versus T (B)  $\frac{1}{k}$  versus T (C)  $\log k$  versus  $1/T$  (D) C versus T
50. Given that K is the rate constant for any order reaction at temperature T, then the value of  $\lim_{T \rightarrow \infty} \log k$  \_\_\_\_\_.  
 (A)  $\frac{A}{2.303}$  (B) A (C)  $2.303 A$  (D)  $\log A$

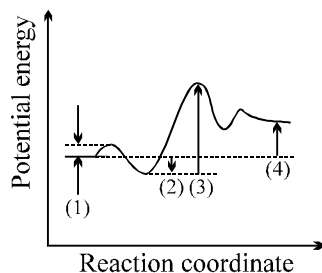
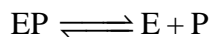
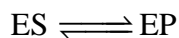
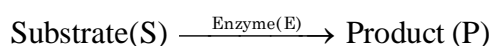
51. For a certain gaseous reaction a  $10^\circ\text{C}$  rise of temperature from  $25^\circ\text{C}$  to  $35^\circ\text{C}$  doubles the rate of reaction. What is the value of activation energy :—
- (A)  $\frac{10}{2.303R \times 298 \times 308}$  (B)  $\frac{2.303 \times 10}{298 \times 308R}$   
 (C)  $\frac{0.693R \times 10}{290 \times 308}$  (D)  $\frac{0.693R \times 298 \times 308}{10}$
52. From the following data, the activation energy (cal/mol) for the reaction  $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$ , is about
- | T (in K) | 1/T, (in, $\text{K}^{-1}$ ) | $\log_{10} k$ |
|----------|-----------------------------|---------------|
| 769      | $1.3 \times 10^{-3}$        | 2.9           |
| 667      | $1.5 \times 10^{-3}$        | 1.1           |
- (A)  $4 \times 10^4$  (B)  $2 \times 10^4$  (C)  $8 \times 10^4$  (D)  $3 \times 10^4$
53. The rate constant, the activation energy and the Arrhenius parameter (A) of a chemical reaction at  $25^\circ\text{C}$  are  $3.0 \times 10^{-4} \text{ s}^{-1}$ ,  $104.4 \text{ kJ mol}^{-1}$  and  $6.0 \times 10^{14} \text{ s}^{-1}$  respectively. The value of the rate constant at  $T \rightarrow \infty$  is
- (A)  $2.0 \times 10^{18} \text{ s}^{-1}$  (B)  $6.0 \times 10^{14} \text{ s}^{-1}$  (C) infinity (D)  $3.6 \times 10^{30} \text{ s}^{-1}$
54. A first order reaction is 50% completed in 20 minutes at  $27^\circ\text{C}$  and in 5 min at  $47^\circ\text{C}$ . The energy of activation of the reaction is
- (A) 100 kJ/mol (B) 55.14 kJ/mol (C) 11.97 kJ/mol (D) 6.65 kJ/mol
55. For the first order reaction  $\text{A} \rightarrow \text{B} + \text{C}$ , carried out at  $27^\circ\text{C}$  if  $3.8 \times 10^{-16} \%$  of the reactant molecules can overcome energy barrier, the  $E_a$  (activation energy) of the reaction is [log 3.8 = 0.58,  $2.303 \times 8.314 \times 17.42 = 333.33$ ]
- (A) 12 kJ/mole (B) 831.4 kJ/mole (C) 100 kJ/mole (D) 111.11 J/mole
56. The following mechanism has been proposed for the exothermic catalyzed complex reaction.



If  $k_1$  is much smaller than  $k_2$ . The most suitable qualitative plot of potential energy (P.E.) versus reaction coordinate for the above reaction.



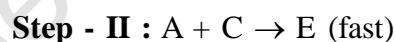
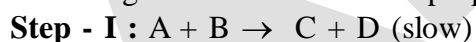
57. Choose the correct set of identifications for the reaction .



- |                                              |                                                      |                                                      |                                                      |
|----------------------------------------------|------------------------------------------------------|------------------------------------------------------|------------------------------------------------------|
| (1)                                          | (2)                                                  | (3)                                                  | (4)                                                  |
| (A) $\Delta E$ for<br>$E + S \rightarrow ES$ | $E_a$ for<br>$ES \rightarrow EP$                     | $\Delta E_{\text{overall}}$<br>for $S \rightarrow P$ | $E_a$ for<br>$EP \rightarrow E + P$                  |
| (B) $E_a$ for<br>$E + S \rightarrow ES$      | $\Delta E$ for<br>$E + S \rightarrow ES$             | $E_a$ for<br>$ES \rightarrow EP$                     | $\Delta E_{\text{overall}}$<br>for $S \rightarrow P$ |
| (C) $E_a$ for<br>$ES \rightarrow EP$         | $E_a$ for<br>$EP \rightarrow E + P$                  | $\Delta E_{\text{overall}}$<br>for $S \rightarrow P$ | $\Delta E$ for<br>$EP \rightarrow E + P$             |
| (D) $E_a$ for<br>$E + S \rightarrow ES$      | $E_a$ for<br>$ES \rightarrow EP$                     | $E_a$ for<br>$EP \rightarrow E + P$                  | $\Delta E_{\text{overall}}$<br>for $S \rightarrow P$ |
| (E) $\Delta E$ for<br>$E + S \rightarrow ES$ | $\Delta E_{\text{overall}}$<br>for $S \rightarrow P$ | $\Delta E$ for<br>$EP \rightarrow E + P$             | $E_a$ for<br>$EP \rightarrow E + P$                  |

#### RATE LAW OF MECHANISM OF REACTION

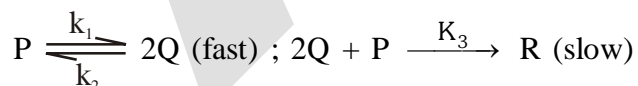
58. Following mechanism has been proposed for a reaction :  $2A + B \rightarrow D + E$



The rate law expression for the reaction is –

- (A)  $r = k[A]^2 [B]$  (B)  $r = k[A] [B]$  (C)  $r = k[A]^2$  (D)  $r = k[A][C]$

59. The reaction mechanism for the reaction  $P \rightarrow R$  is as follows :



the rate law for the main reaction ( $P \rightarrow R$ ) is :

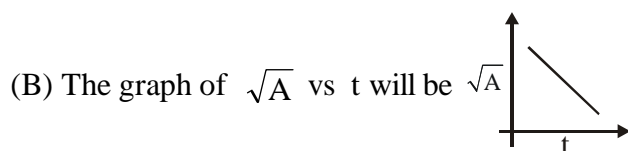
- (A)  $k_1[P] [Q]$  (B)  $k_1k_2[P]$  (C)  $\frac{k_1k_3[P]^2}{k_2}$  (D)  $k_1k_2[a]$
60. The energies of activation for forward and reverse reactions for  $A_2 + B_2 \rightleftharpoons 2AB$  are  $180 \text{ kJ mol}^{-1}$  and  $200 \text{ kJ mol}^{-1}$  respectively. The presence of a catalyst lowers the activation energy of both (forward and reverse) reactions by  $100 \text{ kJ mol}^{-1}$ . The enthalpy change of the reaction ( $A_2 + B_2 \rightarrow 2AB$ ) in the presence of catalyst will be (in  $\text{kJ mol}^{-1}$ ) -
- (A) 300 (B) 120 (C) 280 (D) -20

EXERCISE # (O-2)

MORE THAN ONE MAY BE CORRECT

1. For the reaction  $A \rightarrow B$ , the rate law expression is  $-\frac{d[A]}{dt} = k[A]^{1/2}$ . If initial concentration of  $[A]$  is  $[A]_0$ , then

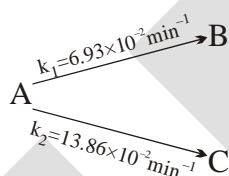
(A) The integrated rate expression is  $k = \frac{2}{t} (A_0^{1/2} - A^{1/2})$



(C) The half life period,  $t_{1/2} = \frac{K}{2[A]_0^{1/2}}$

(D) The time taken for 75% completion of reaction  $t_{3/4} = \frac{\sqrt{[A]_0}}{k}$

2. Consider the reaction,



A, B and C all are optically active compound. If optical rotation per unit concentration of A, B and C are  $60^\circ$ ,  $-72^\circ$ ,  $42^\circ$  and initial concentration of A is 2 M then select correct statement(s).

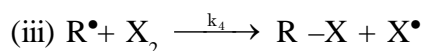
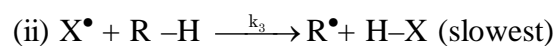
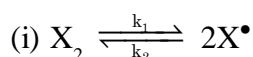
- (A) Solution will be optically active and dextrorotatory after very long time  
 (B) Solution will be optically active and levorotatory after very long time  
 (C) Half life of reaction is 15 min  
 (D) After 75% conversion of A into B and C angle of rotation of solution will be  $36^\circ$ .
3. Select **incorrect** statement(s):

- (A) Unit of pre-exponential factor (A) for second order reaction is  $\text{mol L}^{-1} \text{s}^{-1}$ .  
 (B) A zero order reaction must be a complex reaction.  
 (C) Molecularity is defined only for RDS in a complex reaction.  
 (D) Rate constant (k) remain unaffected on changing temperature.

4. Which of the following is/are **correct** statement?

- (A) Stoichiometry of a reaction tells about the order of the elementary reactions.  
 (B) For a zero order reaction, rate and the rate constant are identical.  
 (C) A zero order reaction is controlled by factors other than concentration of reactants.  
 (D) A zero order reaction is always elementary reaction.

5. For the gas phase reaction :  $R-H + X_2 \rightarrow R-X + HX$ , following mechanism has been proposed



Based on this, select the correct option(s) :-

(A) Effective rate constant for the formation of RX is  $k_3 k_4 \sqrt{\frac{k_1}{k_2}}$

$$(B) \frac{d[RX]}{dt} \propto [X_2]$$

(C) Overall order of the reaction is 3/2

$$(D) \frac{d[RX]}{dt} \propto [RH]^1$$

6. For a first order reaction :  $A(g) \rightarrow 2B(g)$

| Time(in second)                           | 0  | 20  | 40  | $\infty$ |
|-------------------------------------------|----|-----|-----|----------|
| Total pressure of system<br>(in mm.of Hg) | 64 | 112 | 124 | 128      |

(A) Half life of reaction is 10 sec

(B) Value of rate constant for reaction is  $6.93 \times 10^{-3} \text{sec}^{-1}$

(C) Total pressure at  $t = 50$  sec will be 126 mm of Hg

(D) Reaction must be a complex reaction

7. Which of the following is **INCORRECT** for first order reaction ?

(A) On introducing catalyst, both rate constant and rate of reaction increases.

(B) On increasing temperature both rate constant & rate of reaction increases.

(C) On decreasing volume both rate constant & rate of gaseous reaction increases.

(D) On increasing concentration of gaseous reactant at constant volume & constant temperature both total pressure and rate of the reaction increases.

8.  $2X(g) + Y(g) + 3Z(g) \rightarrow \text{Products}$ . The rate equation of above reaction is given by :

Rate =  $K [X]^1 [Y]^0 [Z]^2$ . Choose the correct statements

(A) If  $[Z] \gg [X]$  and 75% of X undergoes reaction in 20 sec, then 50% of X will react in 10 sec. (B)

Rate of reaction decreases by reducing the concentration of Y to half of the original value

(C) The half life of Z increases by increasing its concentration if  $[X] \gg [Z]$

(D) On increasing the concentration of X, Y & Z double, rate of reaction becomes 8 times

9. Select the correct statement -

(A) In a mixture of  $KMnO_4$  &  $H_2C_2O_4$ ,  $KMnO_4$  decolorises faster at higher temperature than lower temperature

(B) A catalyst participate in a chemical reaction by forming temporary bonds with the reactant resulting in an intermediate complex

(C) In collision theory only activation energy determine the criteria for effective collision

(D) Collision theory assumes molecules to be soft spheres & consider their structural aspects.

10. For the reaction  $A + 3B \rightarrow C$ , select the correct statement (s)-  
 (A)  $\frac{d[C]}{dt} = -\frac{d[A]}{dt}$  (B)  $\frac{3d[C]}{dt} = -\frac{d[B]}{dt}$   
 (C) Rate law must be  $r = k[A][B]^3$  (D) Units for rate of reaction are independent of order of reaction
11. Choose the incorrect statement(s) -  
 (A) Activation energy of reaction always decreases on decreasing temperature  
 (B) Order of reaction may change with change in temperature  
 (C) When slowest step is the first step in a mechanism, then the rate law of overall reaction is the same as the rate law for this step  
 (D) Rate of photochemical reaction is directly proportional to intensity of absorbed photons.
12. The forward rate constant of a reaction increases by 7% when its temperature is raised from 300K to 301K while its equilibrium constant increases by 3%. Which of the following is/are correct -  
 (A) Activation energy of forward reaction ( $E_a$ )<sub>F</sub> is  $= 300 \times 301 \times R \times \ln(1.03)$   
 (B) Standard heat of reaction ( $\Delta H^\circ$ ) is  $= 300 \times 301 \times R \times \ln(1.07)$   
 (C) Activation energy of backward reaction ( $E_a$ )<sub>B</sub> is  $= 300 \times 301 \times R \times \ln\left(\frac{1.07}{1.03}\right)$   
 (D) Activation energy of backward reaction ( $E_a$ )<sub>B</sub> is  $= 300 \times 301 \times R \times \ln\left(\frac{1.03}{1.07}\right)$
13. Which statement(s) is/are false ?  
 (A) Every reaction has defined overall order  
 (B) All rate constant have same dimension.  
 (C) Every chemical species that appears in the rate law of reaction must be reactant or product in that reaction.  
 (D) Rate constant is never negative.

### ASSERTION & REASONING TYPE QUESTIONS

14. **Statement-1** : A fractional order reaction must be a complex reaction.  
**Statement-2** : Fractional order of RDS equals to overall order of a complex reaction.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.
15. **Statement-1** : The time of completion of reactions of type  $A \rightarrow \text{product}$  (order  $< 1$ ) may be determined.  
**Statement-2** : Reactions with order  $\geq 1$  are either too slow or too fast and hence the time of completion can not be determined.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.
16. **Statement-1** : In a reversible endothermic reaction, ( $E_{act}$ ) of forward reaction is higher than that of backward reaction  
**Statement-2** : The threshold energy of forward reaction is more than that of backward reaction  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.



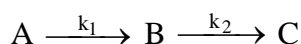
22. Thermal decomposition of compound X is a first order reaction. If 75% of X is decomposed in 100 min. How long will it take for 90% of the compound to decompose?

Given :  $\log 2 = 0.30$

- (A) 190 min (B) 176.66 min (C) 166.66 min (D) 156.66 min
23. Consider a reaction  $A(g) \longrightarrow 3B(g) + 2C(g)$  with rate constant  $1.386 \times 10^{-2} \text{ min}^{-1}$ . Starting with 2 moles of A in 12.5 litre a closed vessel initially, if reaction is allowed to take place at constant pressure & at 298K then find the concentration of B after 100 min.
- (A) 0.04 M (B) 0.36 M (C) 0.09 M (D) None of these

**Paragraph for Question Nos. 24 & 25**

For the given sequential reaction



the concentration of A, B & C at any time 't' is given by

$$[A]_t = [A]_0 e^{-k_1 t} ;$$

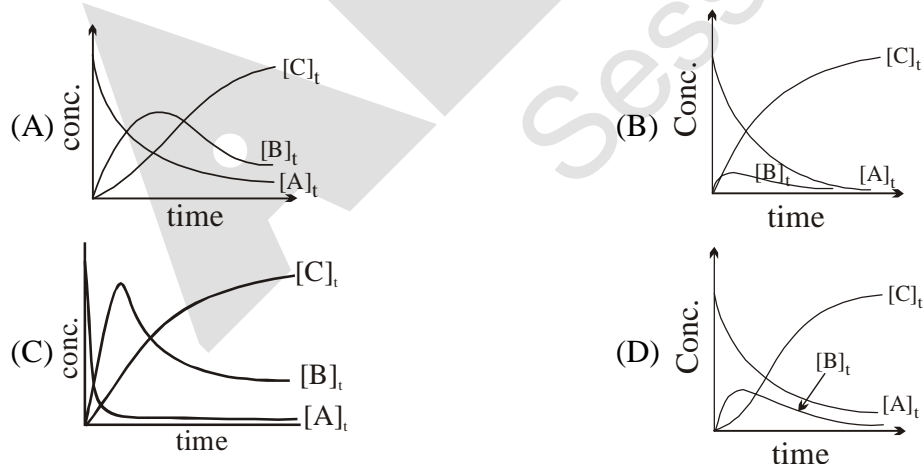
$$[B]_t = \frac{k_1 [A]_0}{(k_2 - k_1)} [e^{-k_1 t} - e^{-k_2 t}]$$

$$[C]_t = [A]_0 - ([A]_t + [B]_t)$$

24. The time at which concentration of B is maximum is

- (A)  $\frac{k_1}{k_2 - k_1}$  (B)  $\frac{1}{k_2 - k_1} \ln \frac{k_1}{k_2}$
- (C)  $\frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2}$  (D)  $\frac{k_2}{k_2 - k_1}$

25. Select the correct graph if  $k_1 = 1000 \text{ s}^{-1}$  and  $k_2 = 20 \text{ s}^{-1}$ .





## MATCH THE COLUMN

26. For the reaction of type  $A(g) \longrightarrow 2B(g)$

**Column-I** contains four entries and **column-II** contains four entries. Entry of column-I are to be matched with **ONLY ONE ENTRY** of column-II

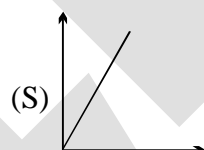
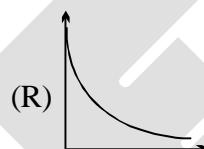
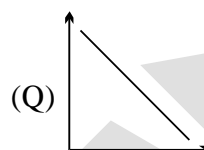
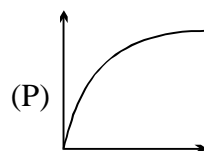
**Column I**

(A)  $\frac{d[B]}{dt}$  vs  $\frac{-d[A]}{dt}$  for first order

(B)  $[A]$  vs  $t$  for first order

(C)  $[B]$  vs  $t$  for first order

(D)  $[A]$  vs  $t$  for zero order

**Column II**

27. Match the column :

**Column-I**

(A) Inversion of cane sugar in excess water.

(B) saponification reaction with 1M NaOH

(C) decomposition of HI on gold

(D) radioactive decay

**Column-II**

(P) not 100% complete

(Q) pseudo-first order

(R) zero order

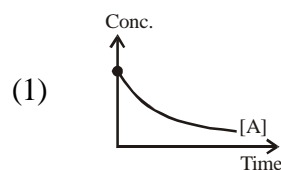
(S) second order

28. For the reaction  $A + B \rightarrow \text{product}$ , Given :  $[A]_0 = [B]_0$

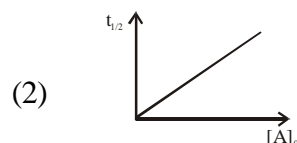
List-I (Observed Rate Law) is -

List-II (Graph)

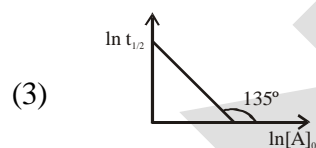
(P)  $r = k[A]$



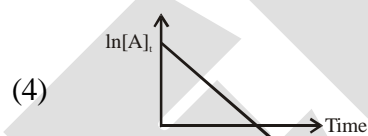
(Q)  $r = k[A]^{1/2}[B]^{1/2}$



(R)  $r = k[A][B]$



(S)  $r = k[A]^0[B]^0$



Code:

|     | P | Q | R | S |
|-----|---|---|---|---|
| (A) | 4 | 1 | 3 | 2 |
| (B) | 2 | 3 | 1 | 4 |
| (C) | 1 | 2 | 3 | 4 |
| (D) | 4 | 3 | 2 | 1 |

Match the Columns for Reaction  $A \rightarrow P$

| Column - I        | Column - II                                                       | Column - III                                                                |
|-------------------|-------------------------------------------------------------------|-----------------------------------------------------------------------------|
| (I) First Order   | (i) Reaction complete in finite time                              | (P) Rate depends on concentration                                           |
| (II) Second Order | (ii) Reaction complete in infinite time                           | (Q) After equal interval of time concentration of reactant left are in G.P. |
| (III) Third Order | (iii) Half life is independent of concentration of reactant       | (R) After equal interval of time concentration of reactant left are in A.P. |
| (IV) Zero Order   | (iv) Half life decreases when concentration of reactant increases | (S) Half life depends on temperature                                        |

29. Select only incorrect option :-

(A) (II), (ii), (P)

(B) (IV), (iii), (R)

(C) (III), (ii), (P)

(D) (I), (ii), (Q)

30. Select only incorrect option :-

(A) (IV), (i), (S)

(B) (III), (iv), (P)

(C) (I), (iv), (Q)

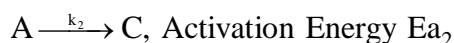
(D) (II), (iv), (S)

## EXERCISE # (J-MAIN)

1. The rate of a chemical reaction doubles for every  $10^\circ\text{C}$  rise of temperature. If the temperature is raised by  $50^\circ\text{C}$ , the rate of the reaction increases by about :- [AIEEE-2011]

(1) 32 times (2) 64 times (3) 10 times (4) 24 times

2. A reactant (1) forms two products : [AIEEE-2011]



If  $E_{a2} = 2 E_{a1}$ , then  $k_1$  and  $k_2$  are related as :-

(1)  $k_1 = 2k_2 e^{E_{a2}/RT}$  (2)  $k_1 = k_2 e^{E_{a1}/RT}$  (3)  $k_2 = k_1 e^{E_{a2}/RT}$  (4)  $k_1 = [A] k_2 e^{E_{a1}/RT}$

3. For the non-stoichiometric reaction  $2A + B \rightarrow C + D$ , the following kinetic data were obtained in three separate experiments, all at 298 K. [J-MAIN 2014]

| Initial Concentration (A) | Initial Concentration (B) | Initial rate of formation of C (mol L <sup>-1</sup> S <sup>-1</sup> ) |
|---------------------------|---------------------------|-----------------------------------------------------------------------|
| 0.1M                      | 0.1M                      | $1.2 \times 10^{-3}$                                                  |
| 0.1M                      | 0.2M                      | $1.2 \times 10^{-3}$                                                  |
| 0.2M                      | 0.1M                      | $2.4 \times 10^{-3}$                                                  |

(1)  $\frac{dc}{dt} = k[A][B]^2$  (2)  $\frac{dc}{dt} = k[A]$  (3)  $\frac{dc}{dt} = k[A][B]$  (4)  $\frac{dc}{dt} = k[A]^2[B]$

4. Higher order (>3) reactions are rare due to :- [JEE-MAIN-(Offline)2015]

(1) shifting of equilibrium towards reactants due to elastic collision  
 (2) loss of active species on collision  
 (3) low probability of simultaneous collision of all the reacting species  
 (4) increase in entropy and activation energy as more molecules are involved.

5. The reaction :  $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$ , follows first order kinetics. The pressure of a vessel containing only  $\text{N}_2\text{O}_5$  was found to increase from 50 mm Hg to 87.5 mm Hg in 30 min. The pressure exerted by the gases after 60 min. will be (Assume temperature remains constant)

(1) 106.25 mm Hg (2) 116.25 mm Hg [JEE-MAIN-(Online)2015]  
 (3) 125 mm Hg (4) 150 mm Hg

6. For the equilibrium,  $A(\text{g}) \rightleftharpoons B(\text{g})$ ,  $\Delta H$  is  $-40 \text{ kJ/mol}$ . If the ratio of the activation energies of the forward ( $E_f$ ) and reverse ( $E_b$ ) reactions is  $\frac{2}{3}$  then :- [JEE-MAIN-(Online)2015]

(1)  $E_f = 60 \text{ kJ/mol}$ ;  $E_b = 100 \text{ kJ/mol}$  (2)  $E_f = 30 \text{ kJ/mol}$ ;  $E_b = 70 \text{ kJ/mol}$   
 (3)  $E_f = 80 \text{ kJ/mol}$ ;  $E_b = 120 \text{ kJ/mol}$  (4)  $E_f = 70 \text{ kJ/mol}$ ;  $E_b = 30 \text{ kJ/mol}$

7. Decomposition of  $\text{H}_2\text{O}_2$  follows a first order reaction. In fifty minutes the concentration of  $\text{H}_2\text{O}_2$  decreases from 0.5 to 0.125 M in one such decomposition. When the concentration of  $\text{H}_2\text{O}_2$  reaches 0.05 M, the rate of formation of  $\text{O}_2$  will be :- **[JEE-MAIN-(Offline)2016]**

(1)  $1.34 \times 10^{-2} \text{ mol min}^{-1}$  (2)  $6.93 \times 10^{-2} \text{ mol min}^{-1}$   
 (3)  $6.93 \times 10^{-4} \text{ mol min}^{-1}$  (4)  $2.66 \text{ L min}^{-1}$  at STP

8. The reaction of ozone with oxygen atoms in the presence of chlorine atoms can occur by a two step process shown below : **[JEE-MAIN-(Online)2016]**

$\text{O}_3(\text{g}) + \text{Cl}(\text{g}) \rightarrow \text{O}_2(\text{g}) + \text{ClO}(\text{g}) \dots\dots(\text{i})$   
 $k_1 = 5.2 \times 10^9 \text{ L mol}^{-1}\text{s}^{-1}$   
 $\text{ClO}(\text{g}) + \text{O}(\text{g}) \rightarrow \text{O}_2(\text{g}) + \text{Cl}(\text{g})$   
 $k_{ii} = 2.6 \times 10^{10} \text{ L mol}^{-1}\text{s}^{-1} \dots\dots(\text{ii})$

The closest rate constant for the overall reaction  $\text{O}_3(\text{g}) + \text{O}(\text{g}) \rightarrow 2\text{O}_2(\text{g})$  is :

(1)  $3.1 \times 10^{10} \text{ L mol}^{-1}\text{s}^{-1}$  (2)  $2.6 \times 10^{10} \text{ L mol}^{-1}\text{s}^{-1}$   
 (3)  $5.2 \times 10^9 \text{ L mol}^{-1}\text{s}^{-1}$  (4)  $1.4 \times 10^{20} \text{ L mol}^{-1}\text{s}^{-1}$

9. Two reactions  $\text{R}_1$  and  $\text{R}_2$  have identical pre-exponential factors. Activation energy of  $\text{R}_1$  exceeds that of  $\text{R}_2$  by  $10 \text{ kJ mol}^{-1}$ . If  $k_1$  and  $k_2$  are rate constants for reactions  $\text{R}_1$  and  $\text{R}_2$  respectively at 300 K, then  $\ln(k_2/k_1)$  is equal to : **[JEE-MAINS-2017]**

( $R = 8.314 \text{ J mol}^{-1}\text{K}^{-1}$ )

(1) 8 (2) 12 (3) 6 (4) 4

10. The rate of a reaction quadruples when the temperature changes from 300 to 310 K. The activation energy of this reaction is (Assume activation energy and pre-exponential factor are independent of temperature ;  $\ln 2 = 0.693$ ,  $R = 8.314 \text{ J mol}^{-1}\text{K}^{-1}$ ) : **[MAINS-2017(online)]**

(1)  $107.2 \text{ kJ mol}^{-1}\text{K}^{-1}$  (2)  $53.6 \text{ kJ mol}^{-1}\text{K}^{-1}$  (3)  $214.4 \text{ kJ mol}^{-1}\text{K}^{-1}$  (4)  $26.8 \text{ kJ mol}^{-1}\text{K}^{-1}$

11. The rate of a reaction A doubles on increasing the temperature from 300 to 310 K. By how much, the temperature of reaction B should be increased from 300 K so that rate doubles if activation energy of the reaction B is twice to that of reaction A : **[MAINS-2017(online)]**

(1) 2.45 K (2) 4.92 K (3) 9.84 K (4) 19.67 K

12. At  $518^\circ \text{C}$ , the rate of decomposition of a sample of gaseous acetaldehyde, initially at a pressure of 363 Torr, was  $1.00 \text{ Torr s}^{-1}$  when 5% had reacted and  $0.5 \text{ Torr s}^{-1}$  when 33% had reacted. The order of the reaction is : **[JEE-MAINS-2018]**

(1) 3 (2) 1 (3) 0 (4) 2

13. For a first order reaction,  $\text{A} \rightarrow \text{P}$ ,  $t_{1/2}$  (half life) is 10 days. The time required for  $\frac{1}{4}$  conversion of A (in days) is :- ( **$\ln 2 = 0.693$ ,  $\ln 3 = 1.1$** ) **[MAINS-2018(online)]**

(1) 5 (2) 4.1 (3) 3.2 (4) 2.5

14.  $\text{N}_2\text{O}_5$  decomposes to  $\text{NO}_2$  and  $\text{O}_2$  and follows first order kinetics. After 50 minutes, the pressure inside the vessel increases from 50 mmHg to 87.5 mmHg. The pressure of the gaseous mixture after 100 minute at constant temperature will be: **[MAINS-2018(online)]**

(1) 116.25 mmHg (2) 175.0 mmHg (3) 106.25 mmHg (4) 136.25 mmHg

15. The following results were obtained during kinetic studies of the reaction :  
 $2A + B \rightarrow \text{Products}$

[MAINS-2019(online)]

| Experiment | [A]<br>(in mol L <sup>-1</sup> ) | [B]<br>(in mol L <sup>-1</sup> ) | Initial Rate of reaction<br>(in mol L <sup>-1</sup> min <sup>-1</sup> ) |
|------------|----------------------------------|----------------------------------|-------------------------------------------------------------------------|
| (I)        | 0.10                             | 0.20                             | $6.93 \times 10^{-3}$                                                   |
| (II)       | 0.10                             | 0.25                             | $6.93 \times 10^{-3}$                                                   |
| (III)      | 0.20                             | 0.30                             | $1.386 \times 10^{-2}$                                                  |

The time (in minutes) required to consume half of A is :

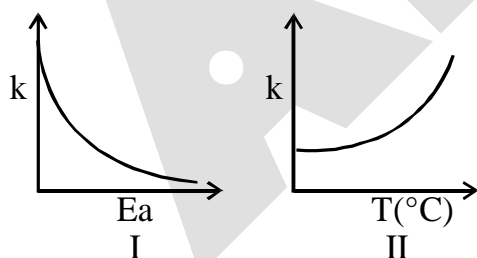
- (1) 10 (2) 5 (3) 100 (4) 1
16. For the reaction,  $2A + B \rightarrow \text{products}$ , when the concentrations of A and B both were doubled, the rate of the reaction increased from  $0.3 \text{ mol L}^{-1}\text{s}^{-1}$  to  $2.4 \text{ mol L}^{-1}\text{s}^{-1}$ . When the concentration of A alone is doubled, the rate increased from  $0.3 \text{ mol L}^{-1}\text{s}^{-1}$  to  $0.6 \text{ mol L}^{-1}\text{s}^{-1}$  [MAINS-2019(online)]

Which one of the following statements is correct ?

- (1) Order of the reaction with respect to B is 2  
 (2) Order of the reaction with respect to A is 2  
 (3) Total order of the reaction is 4  
 (4) Order of the reaction with respect to B is 1
17. For an elementary chemical reaction, [MAINS-2019(online)]

$A_2 \xrightleftharpoons[k_{-1}]{k_1} 2A$ , the expression for  $\frac{d[A]}{dt}$  is :

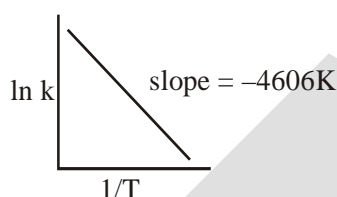
- (1)  $2k_1[A_2] - k_{-1}[A]^2$  (2)  $k_1[A_2] - k_{-1}[A]^2$   
 (3)  $2k_1[A_2] - 2k_{-1}[A]^2$  (4)  $k_1[A_2] + k_{-1}[A]^2$
18. Consider the given plots for a reaction obeying Arrhenius equation ( $0^\circ\text{C} < T < 300^\circ\text{C}$ ) : (k and  $E_a$  are rate constant and activation energy, respectively) [MAINS-2019(online)]



Choose the correct option :

- (1) Both I and II are wrong  
 (2) I is wrong but II is right  
 (3) Both I and II are correct  
 (4) I is right but II is wrong

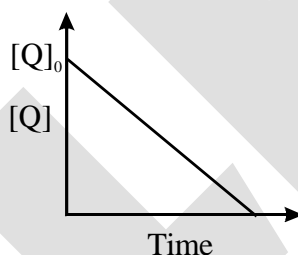
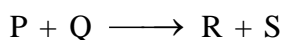
19. The reaction  $2X \rightarrow B$  is a zeroth order reaction. If the initial concentration of X is 0.2 M, the half-life is 6 h. When the initial concentration of X is 0.5 M, the time required to reach its final concentration of 0.2 M will be :-  
 (1) 18.0 h (2) 7.2 h (3) 9.0 h (4) 12.0 h
20. If a reaction follows the Arrhenius equation, the plot  $\ln k$  vs  $\frac{1}{RT}$  gives straight line with a gradient  $(-y)$  unit. The energy required to activate the reactant is : [MAINS-2019(online)]  
 (1) y unit (2)  $-y$  unit (3) yR unit (4) y/R unit
21. For a reaction, consider the plot of  $\ln k$  versus  $1/T$  given in the figure. If the rate constant of this reaction at 400 K is  $10^{-5} \text{ s}^{-1}$ , then the rate constant at 500 K is : [MAINS-2019(online)]



- (1)  $2 \times 10^{-4} \text{ s}^{-1}$  (2)  $10^{-4} \text{ s}^{-1}$  (3)  $10^{-6} \text{ s}^{-1}$  (4)  $4 \times 10^{-4} \text{ s}^{-1}$
22. Decomposition of X exhibits a rate constant of  $0.05 \mu\text{g}/\text{year}$ . How many years are required for the decomposition of  $5 \mu\text{g}$  of X into  $2.5 \mu\text{g}$  ? [MAINS-2019(online)]  
 (1) 50 (2) 25 (3) 20 (4) 40

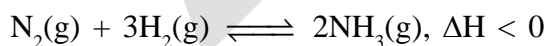
## EXERCISE # (J-ADVANCED)

1. For the first order reaction, [JEE 2011]
- $$2\text{N}_2\text{O}_5(\text{g}) \longrightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$$
- (A) the concentration of the reactant decreases exponentially with time  
 (B) the half-life of the reaction decreases with increasing temperature.  
 (C) the half-life of the reaction depends on the initial concentration of the reactant.  
 (D) the reaction proceeds to 99.6% completion in eight half-life duration.
2. An organic compound undergoes first-order decomposition. The time taken for its decomposition to 1/8 and 1/10 of its initial concentration are  $t_{1/8}$  and  $t_{1/10}$  respectively. What is the value of  $\frac{[t_{1/8}]}{t_{1/10}} \times 10$ ?  
 (take  $\log_{10} 2 = 0.3$ ) [JEE 2012]
3. In the reaction : [JEE 2013]

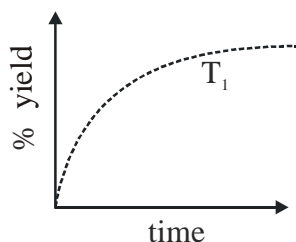


the time taken for 75% reaction of P is twice the time taken for 50% reaction of P. The concentration of Q varies with reaction time as shown in the figure. The overall order of the reaction is -

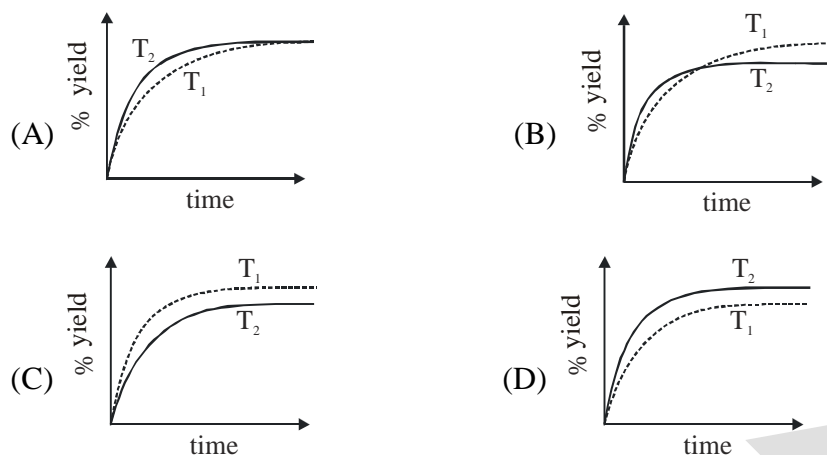
- (A) 2 (B) 3 (C) 0 (D) 1
4. For the elementary reaction  $\text{M} \rightarrow \text{N}$ , the rate of disappearance of **M** increases by a factor of 8 upon doubling the concentration of **M**. The order of the reaction with respect to **M** is  
 (A) 4 (B) 3 (C) 2 (D) 1 [JEE 2014]
5. In dilute aqueous  $\text{H}_2\text{SO}_4$ , the complex diaquodioxalatoferrate(II) is oxidized by  $\text{MnO}_4^-$ . For this reaction, the ratio of the rate of change of  $[\text{H}^+]$  to the rate of change of  $[\text{MnO}_4^-]$  is. [JEE 2015]
6. The % yield of ammonia as a function of time in the reaction [JEE 2015]



at  $(\text{P}, \text{T}_1)$  is given below -



If this reaction is conducted at  $(P, T_2)$ , with  $T_2 > T_1$ , the % yield of ammonia as a function of time is represented by -



7. According to the Arrhenius equation, [JEE 2016]
- (A) A high activation energy usually implies a fast reaction
  - (B) Rate constant increase with increase in temperature. This is due to a greater number of collisions whose energy exceeds the activation energy
  - (C) Higher the magnitude of activation energy, stronger is the temperature dependence of the rate constant
  - (D) The pre-exponential factor is a measure of the rate at which collisions occur, irrespective of their energy.
8. In a bimolecular reaction, the steric factor  $P$  was experimentally determined to be 4.5. The correct option(s) among the following is(are) : [JEE 2017]
- (A) The value of frequency factor predicted by Arrhenius equation is higher than that determined experimentally
  - (B) The activation energy of the reaction is unaffected by the value of the steric factor
  - (C) Since  $P = 4.5$ , the reaction will not proceed unless an effective catalyst is used.
  - (D) Experimentally determined value of frequency factor is higher than that predicted by Arrhenius equation.



## ANSWER-KEY

## EXERCISE # S-I

1. Ans.(i)  $r = \frac{1}{4} \frac{d[\text{NO}]}{dt} = 9 \times 10^{-4} \text{ mol litre}^{-1} \text{ sec}^{-1}$ , (ii)  $3.6 \times 10^{-3} \text{ mol litre}^{-1} \text{ sec}^{-1}$ ,  
(iii)  $5.4 \times 10^{-3} \text{ mol litre}^{-1} \text{ sec}^{-1}$   
$$\text{ROR} = \frac{\text{ROA of NO}}{\text{sto. coeff. of NO}} = \frac{(1.08 \times 10^{-2})/3}{4} = 9 \times 10^{-4} \text{ M sec}^{-1}$$
2. Ans. (i)  $\frac{dx}{dt} = k[A][B]^2$ , (ii) rate increases by 8 times
3. Ans.  $8.33 \times 10^{-6} \text{ Ms}^{-1}$ ,  $0.012 \text{ atm min}^{-1}$
4. Ans. rate increase by 27 times
5. Ans. (a)  $0.019 \text{ L mol}^{-1} \text{ s}^{-1}$ , (b)  $0.038 \text{ L mol}^{-1} \text{ s}^{-1}$
6. Ans. (8)
7. Ans. (2)
8. Ans.  $6 \times 10^{-3} \text{ Ms}^{-1}$
9. Ans.  $1/6$
10. Ans. (i)  $7.2 \text{ M}$ , (ii)  $10 \text{ M}$
11. Ans.  $k = 0.01 \text{ M min}^{-1}$
12. Ans.  $6 \times 10^{-9} \text{ sec}$
13. Ans.  $1.2 \text{ hr}$
14. Ans. (5 atm)
15. Ans. (i) 36 min. (ii) 108 min.
16. Ans. (i)  $0.02 \text{ min}^{-1}$ , (ii) 70 min
17. Ans.  $t = 10 \times t_{1/2}$
18. Ans. 40 month
19. Ans.  $0.02 \text{ min}^{-1}$
20. Ans. 87.5 %
21. Ans. (19)
22. Ans. (20 min)
23. Ans.  $(2 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1})$
24. Ans. 3 hr
25. Ans. 7500 second
26. Ans. (a) Third order, (b)  $r = k[\text{NO}]^2[\text{H}_2]$ , (c)  $7.5 \times 10^{-10} \text{ M sec}^{-1}$ .
27. Ans. (i) first order (ii)  $k = 1.308 \times 10^{-2} \text{ min}^{-1}$  (iii) 73%
28. Ans. (i) Zero order, (ii)  $K = 5 \text{ Pa/s}$
29. Ans. Zero order
30. Ans. (1)
31. Ans.  $k = \frac{1}{t} \ln \frac{P_3}{2(P_3 - P_2)}$
32. Ans.  $k = \frac{1}{t} \ln \frac{r_\infty}{(r_\infty - r_t)}$
33. Ans.  $1.15 \times 10^{-2} \text{ sec}^{-1}$
34. Ans. First order
35. Ans. 240 min.
36. Ans.  $k_1 = 1.55 \times 10^{-2} \text{ min}^{-1}$
37. Ans. 50 sec., 0.1765 atm
38. Ans.  $0.1 \text{ min}^{-1}$
39. Ans. (300 sec.)
40. Ans. (3)
41. Ans.  $\frac{[C]}{[A]} = \frac{10}{11} (e^{11x} - 1)$
42. Ans.  $t = 4 \text{ min}$
43. Ans. 86.625 min
44. Ans.  $t_{1/2} = 36 \text{ min.}$
45. Ans. 10 M
46. Ans. 100 min.
47. Ans. (4 hour)
48. Ans. (6 : 6 : 6 : 1 : 1)
49. Ans. 30 sec.

50. Ans. 50 min,  $\left(\frac{0.2}{e}\right)M$

51. Ans. 5 kJ mol<sup>-1</sup>

52. Ans. 13.44 kcal/mole

53. Ans. 10.28 k cal mol<sup>-1</sup>

54. Ans. (3)

55. Ans. 20 minutes

56. Ans. (10)

57. Ans. (150 K)

58. Ans. (840)

59. Ans. (38.3 kJ mol<sup>-1</sup>)

60. Ans. (20)

61. Ans.  $r = K' [NO]^2 [Br_2]$

62. Ans.  $r = K [NO]^2 [H_2]$ , where  $K = k_2 \times K_1$

63. Ans. (1)

64. Ans. (2)

65. Ans. (rate =  $K_2 K_1 / K_3 [CHCl_3] [Cl_2]^{1/2}$ )

### EXERCISE S-II

- |     |                                        |     |                                    |
|-----|----------------------------------------|-----|------------------------------------|
| 1.  | Ans. 383.2 mm Hg , 403.8 min.          | 2.  | Ans. (50)                          |
| 3.  | Ans. 20 min                            | 4.  | Ans. 315 sec.                      |
| 6.  | Ans. (a) 9.24 kcal/mole, (b) 25.6 hour | 7.  | Ans. $k = 0.0327 \text{ min}^{-1}$ |
| 9.  | Ans. (3)                               | 10. | Ans. (1440 sec)                    |
| 11. | Ans. (5)                               | 12. | Ans. (200 min)                     |
| 13. | Ans. (3)                               | 14. | Ans. (0)                           |
| 15. | Ans. (0.04)                            | 16. | Ans. (8)                           |
| 17. | Ans. (14)                              | 18. | Ans. (1680)                        |
| 19. | Ans. (0)                               | 20. | Ans. (8)                           |

### EXERCISE (O-1)

- |     |         |     |         |     |          |     |         |
|-----|---------|-----|---------|-----|----------|-----|---------|
| 1.  | Ans.(B) | 2.  | Ans.(D) | 3.  | Ans.(C)  | 4.  | Ans.(B) |
| 5.  | Ans.(C) | 6.  | Ans.(C) | 7.  | Ans.(A)  | 8.  | Ans.(C) |
| 9.  | Ans.(D) | 10. | Ans.(C) | 11. | Ans.(A)  | 12. | Ans(D)  |
| 13. | Ans(A)  | 14. | Ans.(C) | 15. | Ans.(A)  | 16. | Ans.(C) |
| 17. | Ans.(D) | 18. | Ans.(D) | 19. | Ans.(A)  | 20. | Ans.(D) |
| 21. | Ans.(B) | 22. | Ans.(A) | 23. | Ans.(D)  | 24. | Ans.(A) |
| 25. | Ans.(D) | 26. | Ans.(C) | 27. | Ans.(A)  | 28. | Ans.(A) |
| 29. | Ans.(C) | 30. | Ans.(C) | 31. | Ans.(C)  | 32. | Ans.(C) |
| 33. | Ans.(B) | 34. | Ans.(C) | 35. | Ans.(C)  | 36. | Ans.(A) |
| 37. | Ans.(D) | 38. | Ans (C) | 39. | Ans.(A)  | 40. | Ans.(C) |
| 41. | Ans.(A) | 42. | Ans (B) | 43. | Ans.(D)  | 44. | Ans.(D) |
| 45. | Ans.(C) | 46. | Ans.(C) | 47. | Ans.(D)  | 48. | Ans.(B) |
| 49. | Ans.(C) | 50. | Ans.(D) | 51. | Ans.(D)  | 52. | Ans.(A) |
| 53. | Ans.(B) | 54. | Ans.(B) | 55. | Ans.(C)  | 56. | Ans.(A) |
| 57. | Ans.(B) | 58. | Ans.(B) | 59. | Ans. (C) | 60. | Ans.(D) |

**EXERCISE # (O-2)**

- |                                                    |                 |                 |                 |
|----------------------------------------------------|-----------------|-----------------|-----------------|
| 1. Ans.(A,B,D)                                     | 2. Ans.(A,D)    | 3. Ans.(A,C, D) | 4. Ans.(A,B,C)  |
| 5. Ans.(C,D)                                       | 6. Ans.(A,C)    | 7. Ans. (C)     | 8. Ans.(A,D)    |
| 9. Ans.(A, B)                                      | 10. Ans.(A,B,D) | 11. Ans. (A)    | 12. Ans.(C)     |
| 13. Ans. (A ,B, C)                                 | 14. Ans.(C)     | 15. Ans.(C)     | 16. Ans.Ans.(C) |
| 17. Ans.(A)                                        | 18. Ans.(B)     | 19. Ans. (A)    | 20. Ans.(B)     |
| 21. Ans.(C)                                        | 22. Ans.(C)     | 23. Ans.(C)     | 24. Ans.(C)     |
| 25. Ans.(C)                                        |                 |                 |                 |
| 26. Ans. (A)→(S) ; (B)→(R) ; (C)→(P), (D)→(Q)      |                 |                 |                 |
| 27. Ans. (A)→(P,Q) ; (B)→(S,P) ; (C)→(R) ; (D)→(P) |                 |                 |                 |
| 28. Ans.(A)                                        | 29. Ans.(B)     | 30. Ans.(C)     |                 |

**EXERCISE # (J-MAIN)**

- |             |             |             |             |
|-------------|-------------|-------------|-------------|
| 1. Ans.(1)  | 2. Ans.(2)  | 3. Ans.(2)  | 4. Ans.(3)  |
| 5. Ans.(1)  | 6. Ans.(3)  | 7. Ans.(3)  | 8. Ans.(3)  |
| 9. Ans.(4)  | 10. Ans.(1) | 11. Ans.(2) | 12. Ans.(4) |
| 13. Ans.(2) | 14. Ans.(3) | 15. Ans.(2) | 16. Ans.(1) |
| 17. Ans.(3) | 18. Ans.(4) | 19. Ans.(1) | 20. Ans.(1) |
| 21. Ans.(2) | 22. Ans.(1) |             |             |

**EXERCISE # (J-ADVANCED)**

- |                |            |                |              |
|----------------|------------|----------------|--------------|
| 1. Ans.(A,B,D) | 2. Ans.(9) | 3. Ans.(D)     | 4. Ans.(B)   |
| 5. Ans.(8)     | 6. Ans.(B) | 7. Ans.(B,C,D) | 8. Ans.(B,D) |

# ELECTROCHEMISTRY

## 1. INTRODUCTION :

Electrochemistry deals with the study of electrical properties of solutions of electrolytes and the inter-relation of chemical phenomenon and electrical energies.

❖ **Electric Conductors are of two types :**

- [illegible]

**(i) Metallic conductors :**

The conductors which conduct electric current by movement of free electrons without undergoing any chemical change are known as metallic conductors.

eg. Metals : Cu, Ag, Fe, Al etc., non metals : graphite and various alloys.

**(ii) Electrolytic conductors :**

Those substances whose aqueous solution conducts the electric current and which are decomposed by the passage of DC current are called electrolytes. In this case, conduction takes place by movement of ions.

Electrolytes also conduct electricity in fused state and undergo decomposition by passage the electric current.

❖ **Strong electrolyte :**

Electrolytes which are completely ionized in aqueous solution or in their molten state, are called ***strong electrolytes***. Their aqueous solutions are strongly conducting.

***Ex : All salts, strong acids and strong bases.***

❖ **Weak electrolyte :**

Electrolytes which are not completely ionized in aqueous solution are called ***Weak electrolytes***. Their aqueous solutions are weakly conducting.

**Ex: Organic acids  $\text{CH}_3\text{COOH}$ ,  $\text{HCN}$  (Except : Alkyl sulphonic acids,  $\text{RSO}_3\text{H}$ )**

**Organic base : Amines, Aniline etc.**

**Note :** Ostwald's dilution law is only applicable for weak electrolytes according to which degree of dissociation ( $\alpha$ ) increases on dilution.

- For weak electrolyte :  $\alpha \ll 1 \Rightarrow$  lesser ions  $\Rightarrow$  weakly conducting
- For strong electrolyte :  $\alpha = 1$  (always)  $\Rightarrow$  more ions  $\Rightarrow$  strongly conducting

❖ **Difference between metallic and electrolytic conduction :**

| <b>Metallic conduction</b>                                                                                                                                    | <b>Electrolytic conduction</b>                                                                                                               |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------|
| <b>(i)</b> Flow of electricity takes place due to free electrons without the decomposition of the substance.                                                  | Flow of electricity takes place by ions.                                                                                                     |
| <b>(ii)</b> No transfer of matter takes place.                                                                                                                | Transfer of matter takes place.                                                                                                              |
| <b>(iii)</b> The resistance to the flow of current increases with the increase in temperature and hence the increase in temperature decreases the conduction. | The resistance to the flow of current decreases with the increase in temperature and hence increase in temperature increases the conduction. |

## 2. ELECTROCHEMICAL CELL :

It is device for inter-converting chemical energy in to electrical energy or vice versa.

**Electrochemical cells are of two types**

### Galvanic cell or Voltaic cell

- A spontaneous chemical reaction generates an electric current | EMF
- Chemical energy converted into electrical energy.

### Electrolytic cell.

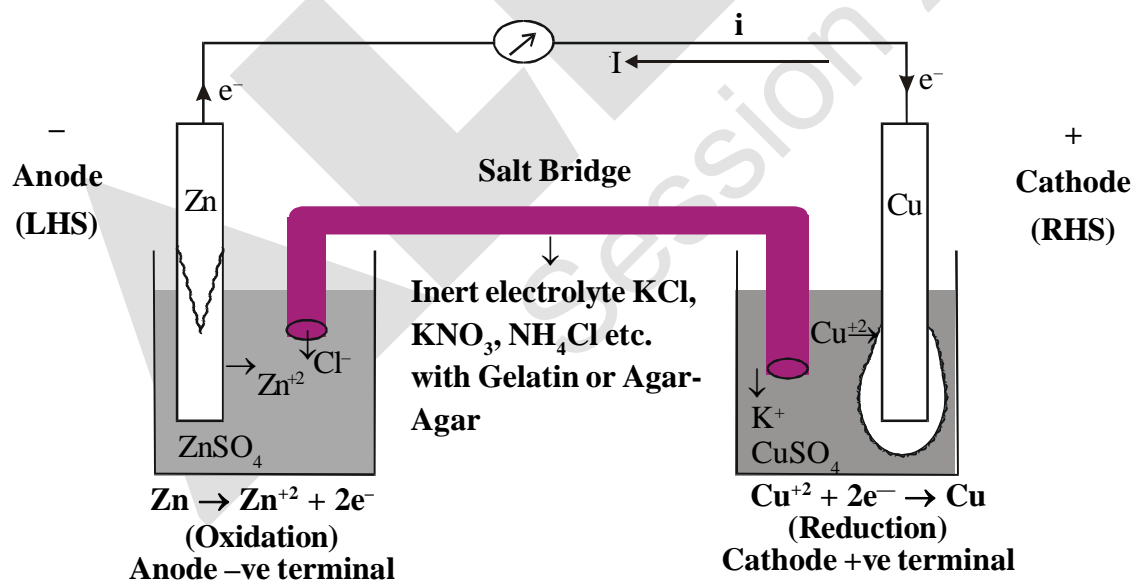
- An electric current drives a non-spontaneous reaction.
- Electrical energy converted into chemical energy.

## 3. GALVANIC CELL | VOLTAIC CELL

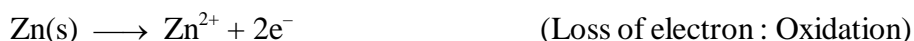
- A cell in which the chemical energy is transformed into electrical energy.
- The chemical reaction occurring in a galvanic cell is a spontaneous redox reaction.
- During the chemical process, the reduction in Gibbs free energy is converted in the form of electrical energy.

$$(\Delta G)_{T,P} = w_{\text{Useful max.}} = -nF E_{\text{cell}}$$

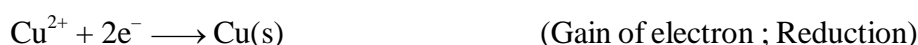
Galvanic cell is made up of two half cells i.e., anodic and cathodic. The cell reaction is of redox kind. Oxidation takes place at anode and reduction at cathode. It may be represented by Daniel cell which is a type of Galvanic cell. Zinc rod immersed in  $\text{ZnSO}_4$  behaves as anode and copper rod immersed in  $\text{CuSO}_4$  behaves as cathode.



❖ **Oxidation takes place at anode :**



❖ **Reduction takes place at cathode :**

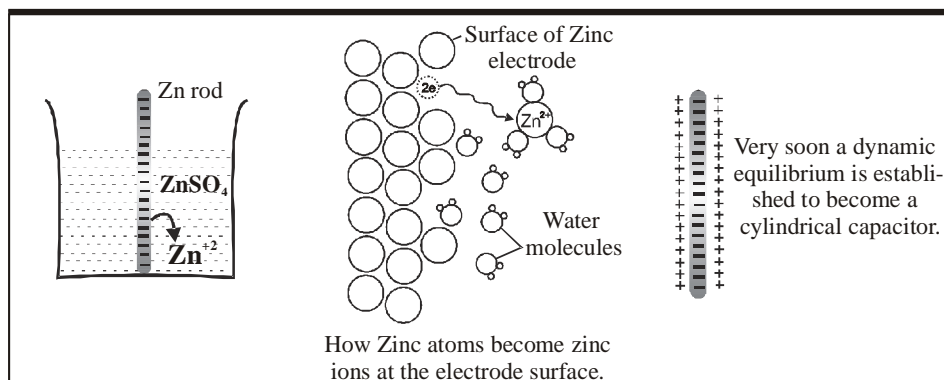


### 3.1 Construction of Cell :

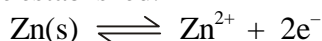
- It has two half-cells, each having a beaker containing a metal strip that dips in its aqueous solution.
- The metal strips are called **electrodes** and are connected by a conducting wire.
- Two solutions are connected by a **salt bridge**.

### 3.2 Construction | Working principle of Daniel cell :

**I. Anode of Daniel cell :** Zn rod is placed in  $\text{ZnSO}_4$  solution are found to have tendency to go into the solution phase when these are placed in contact with their ions or their salt solutions.



The Zn atom or metal atoms will move in the solution to form  $\text{Zn}^{+2}$ . After some time following equilibrium will be established.



There will be accumulation of sufficient negative charge on the rod which will not allow extra zinc ions to move in the solution. i.e. solution will be saturated with  $\text{Zn}^{+2}$  ions.

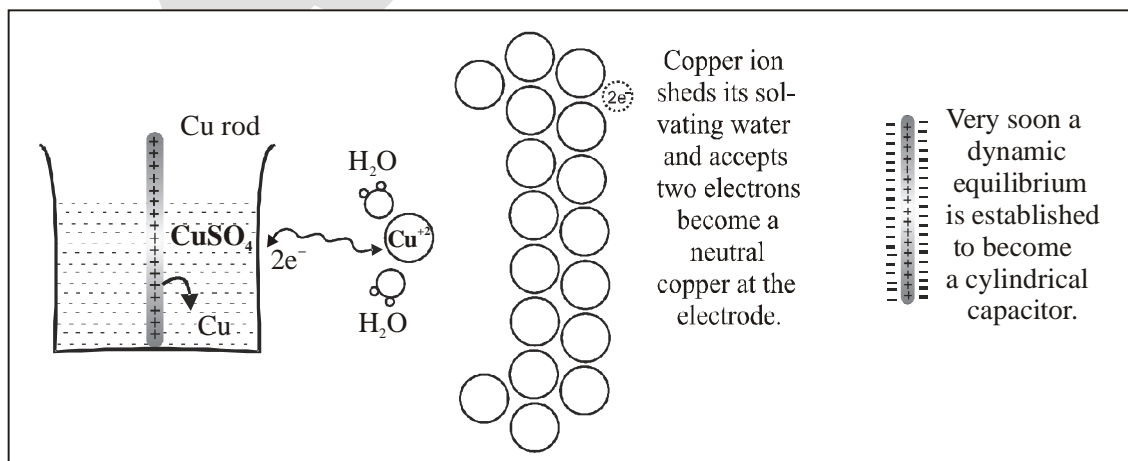
The positive charge will be more concentrated near the rod.

The extra positive charge of the solution will be more concentrated around the negatively charged rod. An electrical double layer is developed in the system and hence a potential difference is created between the rod and the solution which is known as electrode potential

This particular electrode is known as anode :

- At anode oxidation will take place. (Release of electron).
- To act as source of electrons.
- It is of negative polarity.
- The electrode oxidation potential is represented by  $E_{\text{Zn(s)}/\text{Zn}^{2+}_{(\text{aq})}}$  & reduction potential by  $E_{\text{Zn}^{2+}/\text{Zn}}$ .

### II. Cathode of Daniel cell :





❖ **Liquid Junction Potential :**

The potential difference which arises between two solutions when in contact with each other. Salt bridge removes effects of junction potential by providing appropriate migration of ions.

❖ **Characteristics of electrolyte used in salt bridge :**

1. The electrolyte should be inert.
2. The cations and anions of the electrolyte used should be of ionic mobility.
3. Ions of electrolyte should not react with ions involved in cell reaction.

**3.4 Representation of galvanic cell (IUPAC)**

The anode is written on the LHS & cathode on the RHS.

we denote salt bridge by two vertical parallel lines ( $\parallel$ ), if used, in between anode & cathode.

- **Ex.**  $\text{Pt(s)} | \text{H}_2(\text{g}) | \text{H}^+(\text{aq.}) \parallel \text{H}^+(\text{aq.}) | \text{H}_2(\text{g}) | \text{Pt(s)}$
- **Ex.** Daniel cell :  $\text{Zn (s)} | \text{Zn}^{2+}(\text{aq}) \parallel \text{Cu}^{2+}(\text{aq.}) | \text{Cu (s)}$
- **Ex.** For cell reaction :  $\text{H}_2(\text{g}) + \text{Cu}^{+2}(\text{aq}) \longrightarrow 2\text{H}^+(\text{aq}) + \text{Cu(s)}$   
 $\text{Pt} | \text{H}_2(\text{g}) | \text{H}^+(\text{aq}) \parallel \text{Cu}^{2+}(\text{aq.}) | \text{Cu (s)}.$

**3.5 Electrode potential :**

When a strip of metal is brought in contact with the solution containing its own ions then the strip of metal gets positively charged or negatively charged and results into a potential being developed between the metallic strip and its solution which is known as electrode potential.

- **At anode :**  $\text{M} \rightarrow \text{M}^{+n} + n\text{e}^-$  (Oxidation Potential)
- **At cathode :**  $\text{M}^{+n} + n\text{e}^- \rightarrow \text{M}$  (Reduction Potential)
- The value of electrode potential depends upon :
  - (i) the nature of electrode
  - (ii) the concentration of solution
  - (iii) the temperature

**3.6 Standard electrode potential ( $E^\circ$ ) :**

If the concentration of ions is unity, temperature is  $25^\circ\text{C}$  (or any constant temperature) and pressure is 1 bar (standard conditions), the potential of the electrode is called **standard electrode potential**.

- The given value of electrode potential is regarded as reduction potential unless it is specifically mentioned that it is an oxidation potential.

**3.7 Electromotive force of cell or cell voltage :**

The difference in the electrode potentials of the two electrodes of the cell is termed as electro motive force [EMF] or cell voltage which causes current to flow.

$$E_{\text{cell}} = E_{\text{red}}(\text{cathode}) - E_{\text{red}}(\text{anode}) = E_{\text{oxi.}}(\text{anode}) - E_{\text{oxi.}}(\text{cathode}) = E_{\text{oxi.}}(\text{anode}) + E_{\text{red}}(\text{cathode})$$

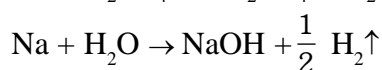
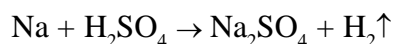


## 3.8 Electro chemical series: Standard aqueous electrode potentials at 298 K

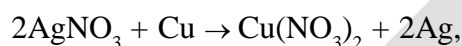
| Electrode Reduction Reaction                                                            | Standard electrode Reduction potential $E^\circ$ , Volts |
|-----------------------------------------------------------------------------------------|----------------------------------------------------------|
| $\text{Li}^+ + e^- \rightarrow \text{Li}$                                               | - 3.05                                                   |
| $\text{K}^+ + e^- \rightarrow \text{K}$                                                 | - 2.93                                                   |
| $\text{Ba}^{+2} + 2e^- \rightarrow \text{Ba}$                                           | - 2.90                                                   |
| $\text{Ca}^{+2} + 2e^- \rightarrow \text{Ca}$                                           | - 2.87                                                   |
| $\text{Na}^+ + e^- \rightarrow \text{Na}$                                               | - 2.71                                                   |
| $\text{Mg}^{+2} + 2e^- \rightarrow \text{Mg}$                                           | - 2.37                                                   |
| $\text{Al}^{+3} + 3e^- \rightarrow \text{Al}$                                           | - 1.66                                                   |
| $\text{Mn}^{+2} + 2e^- \rightarrow \text{Mn}$                                           | - 1.18                                                   |
| $\text{H}_2\text{O} + e^- \rightarrow \frac{1}{2} \text{H}_2 + \text{OH}^-$             | - 0.83                                                   |
| $\text{Zn}^{+2} + 2e^- \rightarrow \text{Zn}$                                           | - 0.76                                                   |
| $\text{Cr}^{+3} + 3e^- \rightarrow \text{Cr}$                                           | - 0.74                                                   |
| $\text{Fe}^{+2} + 2e^- \rightarrow \text{Fe}$                                           | - 0.44                                                   |
| $\text{Cd}^{+2} + 2e^- \rightarrow \text{Cd}$                                           | - 0.40                                                   |
| $\text{Ni}^{+2} + 2e^- \rightarrow \text{Ni}$                                           | - 0.25                                                   |
| $\text{Sn}^{+2} + 2e^- \rightarrow \text{Sn}$                                           | - 0.14                                                   |
| $\text{Pb}^{+2} + 2e^- \rightarrow \text{Pb}$                                           | - 0.13                                                   |
| $2\text{D}^+ + e^- \rightarrow \text{D}_2$                                              | - 0.01 V                                                 |
| $2\text{H}^+ + 2e^- \rightarrow \text{H}_2$                                             | 0                                                        |
| $\text{AgBr(s)} + e^- \rightarrow \text{Ag(s)} + \text{Br}^-$                           | +0.09 V                                                  |
| $\text{AgCl} + e^- \rightarrow \text{Ag} + \text{Cl}^-$                                 | 0.22 V                                                   |
| $\text{Cu}^{+2} + 2e^- \rightarrow \text{Cu}$                                           | + 0.34                                                   |
| $\frac{1}{4} \text{O}_2 + \frac{1}{2} \text{H}_2\text{O} + e^- \rightarrow \text{OH}^-$ | +0.401 V                                                 |
| $\text{I}_2 + 2e^- \rightarrow 2\text{I}^-$                                             | + 0.54                                                   |
| $\text{Q} + 2\text{H}^+ + 1e^- \rightarrow \text{H}_2\text{Q}$                          | + 0.70                                                   |
| $\text{Hg}_2^{+2} + 2e^- \rightarrow 2\text{Hg}$                                        | + 0.79                                                   |
| $\text{Ag}^+ + e^- \rightarrow \text{Ag}$                                               | + 0.80                                                   |
| $\text{Hg}^{+2} + 2e^- \rightarrow \text{Hg}$                                           | + 0.85                                                   |
| $\text{Br}_2 + 2e^- \rightarrow 2\text{Br}^-$                                           | + 1.08                                                   |
| $\frac{1}{4} \text{O}_2 + \text{H}^+ + e^- \rightarrow \frac{1}{2} \text{H}_2\text{O}$  | +1.23 V                                                  |
| $\text{Cl}_2 + 2e^- \rightarrow 2\text{Cl}^-$                                           | + 1.36                                                   |
| $\text{Pt}^{+2} + 2e^- \rightarrow \text{Pt}$                                           | + 1.20                                                   |
| $\text{Au}^{+3} + 3e^- \rightarrow \text{Au}$                                           | + 1.50                                                   |
| $\text{Au}^+ + e^- \rightarrow \text{Au}$                                               | + 1.69                                                   |
| $\text{S}_2\text{O}_8^{--} + 2e^- \rightarrow 2\text{SO}_4^{--}$                        | +2.0 V                                                   |
| $\text{F}_2 + 2e^- \rightarrow 2\text{F}^-$                                             | + 2.87                                                   |

• Application of electrochemical series :

- (i) **Activity of metal** : From electrochemical series, the activity of any metal can easily be determined. All the metals which are placed above hydrogen are stronger reducing agents & can easily evolve  $H_2$  gas whereas metals lying below hydrogen are weaker reducing agents cannot lose electrons to  $H^+$  ions & hence can't evolve  $H_2$  gas. For e.g. Na, K, Zn etc. can easily evolve  $H_2$  whereas Cu, Hg, Ag etc. do not have tendency to evolve  $H_2$  gas.

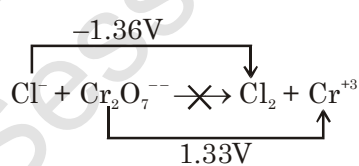
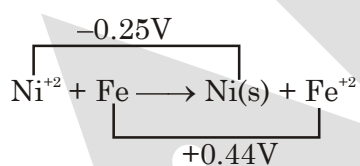


- (ii) **Displacement reaction** : The active metal can easily displace less active metal from their aq. salt solution for e.g. Zn can replace  $Cu^{2+}$  from an aq. solution of  $CuSO_4$ . But Cu cannot displace  $Zn^{2+}$  from solution similarly,

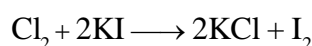
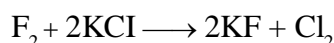


- (iii) **Feasibility of redox reaction** : The feasibility of particular redox reaction can be easily find out from electrochemical series. The metal placed higher or have more reducing property can easily lose electrons to the metal ion present below in series, hence redox reaction become feasible i.e. cell will serve as source of electrical energy. For e.g.  $NiSO_4$  solution cannot be placed in Fe vessel because, the redox reaction between them is feasible.

**Note:** If emf of the cell for redox reaction comes out to be positive, it suggests the redox reaction is spontaneous or feasible. Negative value indicates that redox reaction is not feasible.



- (iv) **Oxidising & reducing powers** : The metals placed above hydrogen in the electrochemical series are strong reducing agents whereas non-metals placed after hydrogen, are strong oxidising agents.
- (v) **Displacement of one non-metal from its salt solution by another non-metal** : A non metal lower in the series will have more reduction potential and will displace another non-metal with lower reduction potential. e.g.  $F_2$  can displace all halide ion from solution.



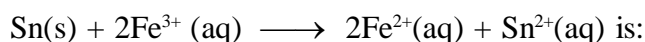
## EXERCISE # I

- For the cell reaction  $2\text{Ce}^{4+} + \text{Co} \longrightarrow 2\text{Ce}^{3+} + \text{Co}^{2+}$   
 $E^\circ_{\text{cell}}$  is 1.89 V. If  $E^\circ_{\text{Co}^{2+}|\text{Co}}$  is  $-0.28$  V, what is the value of  $E^\circ_{\text{Ce}^{4+}|\text{Ce}^{3+}}$  ?
- Determine the standard reduction potential for the half reaction :  
 $\text{Cl}_2 + 2\text{e}^- \longrightarrow 2\text{Cl}^-$   
 Given  $\text{Pt}^{2+} + 2\text{Cl}^- \longrightarrow \text{Pt} + \text{Cl}_2$ ,  $E^\circ_{\text{cell}} = -0.15$  V  
 $\text{Pt}^{2+} + 2\text{e}^- \longrightarrow \text{Pt}$   $E^\circ = 1.20$  V
- Is 1.0 M  $\text{H}^+$  solution under  $\text{H}_2\text{SO}_4$  at 1.0 atm capable of oxidising silver metal in the presence of 1.0 M  $\text{Ag}^+$  ion?  
 $E^\circ_{\text{Ag}^+|\text{Ag}} = 0.80$  V,  $E^\circ_{\text{H}^+|\text{H}_2(\text{Pt})} = 0.0$  V
- If  $E^\circ_{\text{Fe}^{2+}|\text{Fe}} = -0.44$  V,  $E^\circ_{\text{Fe}^{3+}|\text{Fe}^{2+}} = 0.77$  V. Calculate  $E^\circ_{\text{Fe}^{3+}|\text{Fe}}$ .
- Which of the following statement is wrong about galvanic cell ?  
 (A) cathode is positive charged (B) anode is negatively charged  
 (C) reduction takes place at the anode (D) reduction takes place at the cathode
- A standard reduction electrode potentials of four metal cations are -  
 $\text{A}^+ = -0.250$  V,  $\text{B}^+ = -0.140$  V  $\text{C}^+ = -0.126$  V,  $\text{D}^+ = -0.402$  V  
 The metal that displaces  $\text{A}^+$  from its aqueous solution is :-  
 (A) B (B) C (C) D (D) None of the above
- The standard reduction potentials for two half-cell reactions are given below,  
 $\text{Cd}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cd}(\text{s})$ ,  $E^\circ = -0.40$  V  
 $\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$ ,  $E^\circ = 0.80$  V  
 The standard free energy change for the reaction  
 $2\text{Ag}^+(\text{aq}) + \text{Cd}(\text{s}) \rightarrow 2\text{Ag}(\text{s}) + \text{Cd}^{2+}(\text{aq})$  is given by :  
 (A) 115.8 KJ (B) -115.8 KJ (C) -231.6 KJ (D) 231.6 KJ
- The reduction potential values are given below:  
 $\text{Al}^{3+}|\text{Al} = -1.67$  volt,  $\text{Mg}^{2+}|\text{Mg} = -2.34$  volt  
 $\text{Cu}^{2+}|\text{Cu} = +0.34$  volt,  $\text{I}_2|\text{I}^- = +0.53$  volt  
 Which one is the best reducing agent ?  
 (A) Al (B) Mg (C) Cu (D)  $\text{I}_2$
- Standard reduction electrode potentials of three metals A, B and C are respectively + 0.5V, - 3.0V and -1.2 V. The reducing powers of these metals are : **[AIEEE 2003]**  
 (A)  $\text{C} > \text{B} > \text{A}$  (B)  $\text{A} > \text{C} > \text{B}$  (C)  $\text{B} > \text{C} > \text{A}$  (D)  $\text{A} > \text{B} > \text{C}$
- The  $E^\circ_{\text{M}^{3+}/\text{M}^{2+}}$  values for Cr, Mn, Fe and Co are  $-0.41$ ,  $+1.57$ ,  $+0.77$  and  $+1.97$  V respectively. For which one of these metals the change in oxidation state from +2 to +3 is easiest ?  
 (A) Fe (B) Mn (C) Cr (D) Co **[AIEEE 2004]**

11. Consider the following  $E^0$  values, [AIEEE 2004]

$$E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 = +0.77\text{V} \quad E_{\text{Sn}^{2+}/\text{Sn}}^0 = -0.14\text{V}$$

Under standard conditions the potential for the reaction,



- (A) 0.91V (B) 1.40V (C) 1.68V (D) 0.63V

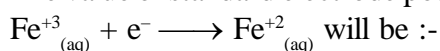
12. For a spontaneous reaction the  $\Delta G$ , equilibrium constant (K) and  $E_{\text{Cell}}^0$  will be respectively

[AIEEE 2005]

- (A) -ve, < 1, -ve (B) -ve, > 1, -ve (C) -ve, > 1, +ve (D) +ve, > 1, -ve

13. Given:  $E_{\text{Fe}^{3+}/\text{Fe}}^0 = -0.036\text{V}$ ,  $E_{\text{Fe}^{2+}/\text{Fe}}^0 = -0.439\text{V}$

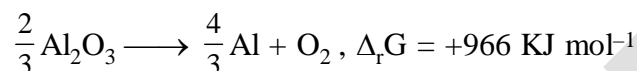
The value of standard electrode potential for the change.



[AIEEE 2009]

- (A) 0.770 V (B) -0.27 V (C) -0.072 V (D) 0.385 V

14. The Gibbs energy for the decomposition of  $\text{Al}_2\text{O}_3$  at  $500^\circ\text{C}$  is as follows [AIEEE 2010]



The potential difference needed for electrolytic reduction of  $\text{Al}_2\text{O}_3$  at  $500^\circ\text{C}$  is at least :-

- (A) 5.0 V (B) 4.5 V (C) 3.0 V (D) 2.5 V

15. A standard hydrogen electrode has zero electrode potential because

- (A) hydrogen is easier to oxidise (B) electrode potential is assumed to be zero  
(C) hydrogen atom has only one electron (D) hydrogen is the lightest element.

16.  $E^0$  for  $\text{F}_2 + 2\text{e}^- = 2\text{F}^-$  is 2.8 V,  $E^0$  for  $\frac{1}{2}\text{F}_2 + \text{e}^- = \text{F}^-$  is ?

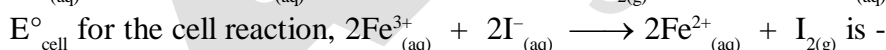
- (A) 2.8 V (B) 1.4 V (C) -2.8 V (D) -1.4 V

17. If  $\Delta G^0$  of the cell reaction,  $\text{AgCl(s)} + \frac{1}{2}\text{H}_2(\text{g}) \rightarrow \text{Ag(s)} + \text{H}^+ + \text{Cl}^-$  is -21.52 KJ

then  $\Delta G^0$  of  $2\text{AgCl(s)} + \text{H}_2(\text{g}) \rightarrow 2\text{Ag(s)} + 2\text{H}^+ + 2\text{Cl}^-$  is :

- (A) -21.52 KJ (B) -10.76 KJ (C) -43.04 KJ (D) 43.04 KJ

18. Given electrode potentials :



- (A)  $(2 \times 0.771 - 0.536) = 1.006 \text{ volts}$  (B)  $(0.771 - 0.5 \times 0.536) = 0.503 \text{ volts}$   
(C)  $0.771 - 0.536 = 0.235 \text{ volts}$  (D)  $0.536 - 0.771 = -0.235 \text{ volts}$

### 3.9 NERNST EQUATION :

For a reaction  $a\text{A} + b\text{B} = c\text{C} + d\text{D}$

$$\Delta G = \Delta G^0 + RT \ln Q$$

$$-nFE = -nFE^0 + RT \ln Q$$

With the help of Nernst equation, we can calculate the non-standard electrode potential of electrode or EMF of cell.

**Nernst equation predicts effects of concentration, pressure or temperature changes on cell EMF.**

Nernst equation can be applied on half-cell as well as complete Galvanic cells reaction.

Nernst equation can be applied on half-cell as well as complete Galvanic cells reaction.

$$E_{\text{cell}} = E^{\circ} - \frac{RT}{nF} \ln Q = E^{\circ} - \frac{2.303RT}{nF} \log Q$$

Where -

$E^{\circ}$  = Standard electrode potential

R = Gas constant

T = Temperature (in K)

F = Faraday (96500 coulomb  $\text{mol}^{-1}$ )

n = No. of  $e^{-}$  gained or lost in balanced equation.

Q = Reaction quotient

$$\frac{2.303 \times 8.314 \times 298}{96500} = 0.059 \text{ volt (At 298 K)}$$

**Note:** (i) For writing Nernst equation, first write balanced cell reaction.

(ii) Nernst equation can be applied on half-cell as well as complete Galvanic cells.

### 3.10 THERMODYNAMIC TREATMENT OF CELL :

(i) **Determination of equilibrium constant :** We know, that

$$E = E^{\circ} - \frac{0.0591}{n} \log Q \quad \dots(i)$$

At equilibrium, the cell potential is zero because cell reactions are balanced, i.e.  $E = 0$  &  $Q = K_{\text{eq}}$ .

$\therefore$  From E (i), we have

$$0 = E^{\circ} - \frac{0.0591}{n} \log K_{\text{eq}} \quad \text{or} \quad K_{\text{eq}} = \text{anti log} \left[ \frac{nE^{\circ}}{0.0591} \right] = 10^{\frac{nE^{\circ}}{0.591}}$$

(ii) **Heat of Reaction inside the cell:** Let n Faraday charge flows out of a cell of e.m.f. E, then

$$-\Delta G = nFE \quad (i)$$

Gibbs Helmholtz equation (from thermodynamics) may be given as,

$$\Delta G = \Delta H + T \left[ \frac{\partial \Delta G}{\partial T} \right]_p \quad (ii)$$

From Eqs. (i) and (ii), we have

$$-nFE = \Delta H + T \left[ \frac{\partial (-nFE)}{\partial T} \right]_p = \Delta H - nFT \left[ \frac{\partial E}{\partial T} \right]_p$$

$$\therefore \Delta H = -nFE + nFT \left[ \frac{\partial E}{\partial T} \right]_p$$

(iii) **Entropy change inside the cell :** We know that  $G = H - TS$  or  $\Delta G = \Delta H - T\Delta S$  ... (i)

where  $\Delta G$  = Free energy change ;  $\Delta H$  = Enthalpy change and  $\Delta S$  = entropy change.

According to Gibbs Helmholtz equation,

$$\Delta G = \Delta H + T \left[ \frac{\partial \Delta G}{\partial T} \right]_p \quad \dots (ii)$$

From Eqs. (i) and (ii), we have

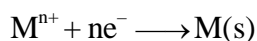
$$-T\Delta S = T \left[ \frac{\partial \Delta G}{\partial T} \right]_p \quad \text{or} \quad \Delta S = - \left[ \frac{\partial \Delta G}{\partial T} \right]_p$$

$$\text{or} \quad \Delta S = nF \left[ \frac{\partial E}{\partial T} \right]_p$$

where  $\left[ \frac{\partial E}{\partial T} \right]_p$  is called temperature coefficient of cell.

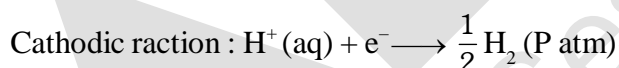
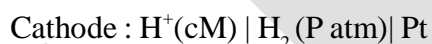
### 3.11 DIFFERENT TYPES OF ELECTRODES

#### I. Metal - Metal ion electrode : Ex. - $M^{n+} | M$



$$E_{M^{n+}/M} = E_{M^{n+}/M}^0 - \frac{0.059}{n} \log \frac{1}{[M^{n+}]}$$

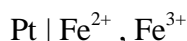
#### II. Gas - ion Electrode :



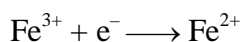
$$E = E^0 - 0.0591 \log \frac{P_{H_2}^{1/2}}{[H^+]} = -0.0591 \text{ pH} \left[ \because E_{H^+/H_2}^0 = 0 \text{ \& } pH_2 = 1 \text{ bar} \right]$$

#### III. Oxidation - reduction Electrode (or redox electrode) :

It has same metal (or element) in two different oxidation states in same solution.



As a reduction electrode



$$E = E^0 - 0.0591 \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

Also,  $\text{Pt} | \text{Cr}_2\text{O}_7^{2-}(\text{aq.}), \text{Cr}^{+3}(\text{aq.}), \text{H}^+$   
 $\text{Pt} | \text{Mn}^{+2}(\text{aq.}), \text{MnO}_4^-(\text{aq.}), \text{H}^+$

#### IV. Metal - metal insoluble salt-anion electrode :

In this half cell, a metal coated with its insoluble salt is in contact with a solution containing the anion of the insoluble salt. eg. Silver-Silver Chloride Half Cell:

This half cell is represented as  $\text{Cl}^- | \text{AgCl} | \text{Ag}$ . The equilibrium reaction that occurs at the electrode is

$$\text{AgCl}(\text{s}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s}) + \text{Cl}^-(\text{aq})$$

$$E_{\text{Cl}^- / \text{AgCl} / \text{Ag}}^0 = E_{\text{Ag}^+ / \text{Ag}}^0 + \frac{0.0591}{1} \log K_{\text{sp}}$$

$$E_{\text{Cl}^- / \text{AgCl} / \text{Ag}} = E_{\text{Cl}^- / \text{AgCl} / \text{Ag}}^0 - \frac{0.0591}{1} \log [\text{Cl}^-]$$

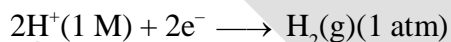
potential of such cells depends upon the concentration of anions. Such cells can be used as **Reference Electrode**.

#### 3.12 Reference Electrode :

Absolute values of electrode potentials can not be measured. Reference electrodes is an electrode used to measure the electrode potential of other electrodes.

##### (a) Standard Hydrogen Electrode (SHE) :

It consist of a platinum electrode over which  $\text{H}_2$  gas (1 bar pressure) is bubbled and the electrode is immersed in a solution that is 1 M in  $\text{H}^+$  at any specified temperature.

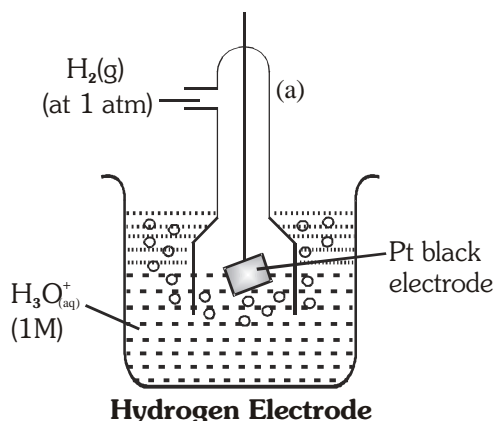


The potential of this electrode at all temperature is taken as Zero volt.

[IUPAC convention :  $E_{\text{H}^+ / \text{H}_2}^0 = E_{\text{H}_2 / \text{H}^+}^0 = 0$ ]

#### Calculation of electrode potential :

| At Anode                                                                                                                                                                                                                                                                                        | At Cathode                                                                                                                                                                                                                                                                                   |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| $\text{H}_2(\text{g}) \rightleftharpoons 2\text{H}^+ + 2\text{e}^-$                                                                                                                                                                                                                             | $2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g})$                                                                                                                                                                                                                          |
| <ul style="list-style-type: none"> <li>Oxidation potential O.P. = <math>E_{\text{H}_2(\text{g}) / \text{H}^+(\text{aq.})}</math></li> <li><math>E_{\text{H}_2(\text{g}) / \text{H}^+(\text{aq.})}^0 = \text{SOP} = 0</math></li> <li><math>E_{\text{H}_2 / \text{H}^+} \neq 0</math></li> </ul> | <ul style="list-style-type: none"> <li>Reduction Potential (R.P.)</li> <li><math>E_{\text{H}^+ / \text{H}_2(\text{g})} = \text{RP}</math></li> <li><math>E_{\text{H}^+ / \text{H}_2(\text{g})}^0 = \text{SRP} = 0</math></li> <li><math>E_{\text{H}^+ / \text{H}_2} \neq 0</math></li> </ul> |



- To calculate standard potential of any other electrode a cell is coupled with standard hydrogen electrode (SHE) and its potential is measured that gives the value of electrode potential of that electrode.

**Ex. Anode :** Zinc electrode

**Cathode :** SHE

**Cell :** Zinc electrode || SHE

$$E_{\text{cell}} = E_{\text{H}^+/\text{H}_2(\text{g})} - E_{\text{Zn}^{2+}/\text{Zn}}^{\circ}$$

$$= 0.76 \text{ V} \quad (\text{at } 298 \text{ K experimentally})$$

So,  $E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = -0.76 \text{ V (SRP)}$

$E_{\text{Zn}|\text{Zn}^{2+}(\text{aq})}^{\circ} = 0.76 \text{ V (SOP)}$

**(b) Calomel Electrode :**

**Cathode :**  $\text{Cl}^-(\text{c M}) | \text{Hg}_2\text{Cl}_2(\text{s}) | \text{Hg}(\text{l}) | \text{Pt}(\text{s})$

It is prepared by a Pt wire in contact with a paste of Hg and  $\text{Hg}_2\text{Cl}_2$  present in a KCl solution.

reaction  $\text{Hg}_2\text{Cl}_2(\text{s}) + 2\text{e}^- \longrightarrow 2\text{Hg}(\text{l}) + 2\text{Cl}^-$ ;  $E^{\circ} = +0.27 \text{ V}$

$$\Rightarrow E_{\text{Cl}^-/\text{Hg}_2\text{Cl}_2/\text{Hg}} = E_{\text{Cl}^-/\text{Hg}_2\text{Cl}_2/\text{Hg}}^{\circ} - \frac{0.059}{2} \log[\text{Cl}^-]^2$$

#### 4. CONCENTRATION CELL

The cells in which electrical current is produced due to transport of a substance from higher to lower concentration. Concentration gradient may arise either in electrode material or in electrolyte. Thus there are two types of concentration cells.

##### 4.1 Electrode concentration cell :

$\text{Pt}, \text{H}_2(\text{P}_1) | \text{H}^+(\text{C}) | \text{H}_2(\text{P}_2), \text{Pt}$

Here, hydrogen gas is bubbled at two different partial pressures at electrode dipped in the solution of same electrolyte.

**Cell process :**  $1/2\text{H}_2(\text{P}_1) \rightarrow \text{H}^+(\text{c}) + \text{e}^-$  (Anode process)

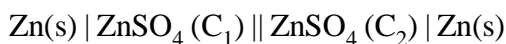
$$\frac{\text{H}^+(\text{c}) + \text{e}^- \rightarrow 1/2\text{H}_2(\text{P}_2)}{1/2\text{H}_2(\text{P}_1) \rightleftharpoons 1/2\text{H}_2(\text{P}_2)} \quad \therefore E = -\frac{2.303RT}{F} \log \left[ \frac{\text{P}_2}{\text{P}_1} \right]^{1/2}$$



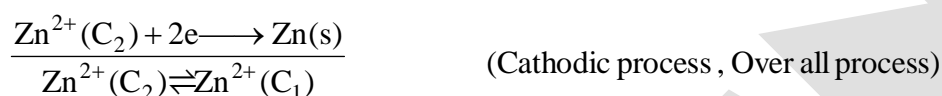
$$\text{or } E = \left[ \frac{2.303RT}{2F} \right] \log \left[ \frac{p_2}{p_1} \right], \text{ At } 25^\circ\text{C}, E = \frac{0.059}{2F} \log \left[ \frac{p_1}{p_2} \right]$$

For spontaneity of such cell reaction,  $p_1 > p_2$

#### 4.2 Electrolyte concentration cells:



In such cells, concentration gradient arise in electrolyte solutions. Cell process may be given as,



$\therefore$  From Nernst equation, we have

$$E = 0 - \frac{2.303RT}{2F} \log \left[ \frac{C_1}{C_2} \right] \quad \text{or} \quad E = \frac{2.303RT}{2F} \log \left[ \frac{C_2}{C_1} \right]$$

For spontaneity of such cell reaction,  $C_2 > C_1$

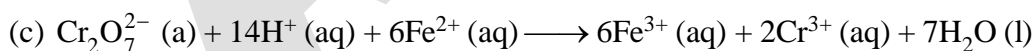
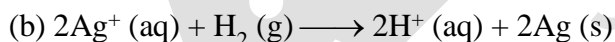
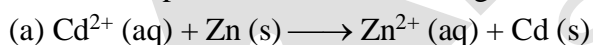
### EXERCISE # II

#### Representation of Cell diagrams, complete and half cell reactions :

19. Write cell reaction of the following cells :



20. Write cell representation for following cells.



21. Calculate the EMF of a Daniel cell when the concentration of  $\text{ZnSO}_4$  and  $\text{CuSO}_4$  are 0.001 M and 0.1M respectively. The standard potential of the cell is 1.1V.

22. Calculate  $E^0$  and  $E$  for the cell  $\text{Sn} \mid \text{Sn}^{2+} (1\text{M}) \parallel \text{Pb}^{2+} (10^{-3}\text{M}) \mid \text{Pb}$ ,  $E^0 (\text{Sn}^{2+} \mid \text{Sn}) = -0.14\text{V}$ ,  $E^0 (\text{Pb}^{2+} \mid \text{Pb}) = -0.13\text{V}$ . Is cell representation is correct?

23. At what concentration of  $\text{Cu}^{2+}$  in a solution of  $\text{CuSO}_4$  will the electrode potential be zero at  $25^\circ\text{C}$ ? Given :  $E^0 (\text{Cu} \mid \text{Cu}^{2+}) = -0.34 \text{ V}$ .

24. Calculate the equilibrium constant for the reaction





37. For a reaction -  $A(s) + 2B_{(aq)}^+ \rightarrow A_{(aq)}^{2+} + 2B_{(s)}$   $K_C$  has been found to be  $10^{12}$ . The  $E^\circ_{\text{cell}}$  is:  
 (A) 0.354 V (B) 0.708 V (C) 0.0098 V (D) 1.36 V
38. At  $25^\circ\text{C}$  the standard emf of cell having reactions involving two electrons change is found to be 0.295V. The equilibrium constant of the reaction is -  
 (A)  $29.5 \times 10^{-2}$  (B) 10 (C)  $10^{10}$  (D)  $29.5 \times 10^{10}$
39. For the cell reaction  

$$\text{Mg}_{(s)} + \text{Zn}^{2+}_{(aq)} (1\text{M}) \longrightarrow \text{Zn}_{(s)} + \text{Mg}^{2+}_{(aq)} (1\text{M})$$
 The emf has been found to be 1.60 V,  $E^\circ$  of the cell is :  
 (A) -1.60 V (B) 1.60 V (C) 0.0 V (D) 0.16 V
40. The emf of the cell in which the following reaction,  

$$\text{Zn}_{(s)} + \text{Ni}^{2+}_{(aq)} (a = 0.1) \rightarrow \text{Zn}^{2+}_{(aq)} (a = 1.0) + \text{Ni}_{(s)}$$
 occurs, is found to be 0.5105 V at 298 K. The standard e.m.f. of the cell is :-  
 (A) -0.5105 V (B) 0.5400 V (C) 0.4810 V (D) 0.5696 V
41. Given electrode potentials :  

$$\text{Fe}^{3+}_{(aq)} + e^- \longrightarrow \text{Fe}^{2+}_{(aq)} ; E^\circ = 0.771 \text{ volts} \quad \text{I}_{2(g)} + 2e^- \longrightarrow 2\text{I}^{-}_{(aq)} ; E^\circ = 0.536 \text{ volts}$$
 $E^\circ_{\text{cell}}$  for the cell reaction,  

$$2\text{Fe}^{3+}_{(aq)} + 2\text{I}^{-}_{(aq)} \longrightarrow 2\text{Fe}^{2+}_{(aq)} + \text{I}_{2(g)}$$
 is -  
 (A)  $(2 \times 0.771 - 0.536) = 1.006$  volts  
 (B)  $(0.771 - 0.5 \times 0.536) = 0.503$  volts  
 (C)  $0.771 - 0.536 = 0.235$  volts  
 (D)  $0.536 - 0.771 = -0.235$  volts
42. For the redox reaction :  

$$\text{Zn}_{(s)} + \text{Cu}^{2+} (0.1\text{M}) \rightarrow \text{Zn}^{2+} (1\text{M}) + \text{Cu}_{(s)}$$
 taking place in a cell,  
 $E^\circ_{\text{cell}}$  is 1.10 volt.  $E_{\text{cell}}$  for the cell will be  $\left(2.303 \frac{RT}{F} = 0.0591\right)$  [AIEEE 2003]  
 (A) 1.07 volt (B) 0.82 volt (C) 2.14 volt (D) 1.80 volt
43. For a cell reaction involving a two-electron change, the standard e.m.f. of the cell is found to be 0.295V at  $25^\circ\text{C}$ . The equilibrium constant of the reaction at  $25^\circ\text{C}$  will be : [AIEEE 2003]  
 (A) 10 (B)  $1 \times 10^{10}$  (C)  $1 \times 10^{-10}$  (D)  $29.5 \times 10^{-2}$
44. In a cell that utilises the reaction, [AIEEE 2004]  

$$\text{Zn}_{(s)} + 2\text{H}^+_{(A)} \longrightarrow \text{Zn}^{2+}_{(aq)} + \text{H}_{2(g)}$$
 addition of  $\text{H}_2\text{SO}_4$  to cathode compartment, will :  
 (A) increase the  $E_{\text{cell}}$  and shift equilibrium to the right  
 (B) lower the  $E_{\text{cell}}$  and shift equilibrium to the right  
 (C) lower the  $E_{\text{cell}}$  and shift equilibrium to the left  
 (D) increase the  $E_{\text{cell}}$  and shift equilibrium to the left

45. The standard e.m.f. of a cell, involving one electron change is found to be 0.591 V at 25°C. The equilibrium constant of the reaction is ( $F = 96,500 \text{ C mol}^{-1}$ ;  $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ ) [AIEEE 2004]  
 (A)  $1.0 \times 10^{10}$  (B)  $1.0 \times 10^5$  (C)  $1.0 \times 10^1$  (D)  $1.0 \times 10^{30}$
46. Given :  $E_{\text{Cr}^{3+}/\text{Cr}}^0 = -0.72 \text{ V}$ ,  $E_{\text{Fe}^{2+}/\text{Fe}}^0 = -0.42 \text{ V}$ . The potential for the cell [AIEEE 2008]  
 $\text{Cr}_{(s)} | \text{Cr}^{3+}_{(aq)} (0.1 \text{ M}) || \text{Fe}^{2+}_{(aq)} (0.01 \text{ M}) | \text{Fe}_{(s)}$  is  
 (A) 0.26 V (B) 0.339 V (C) -0.339 V (D) -0.26 V
47. The cell  $\text{Zn} | \text{Zn}^{2+}_{(aq)} (1 \text{ M}) || \text{Cu}^{2+}_{(aq)} (1 \text{ M}) | \text{Cu}$  ( $E_{\text{cell}}^0 = 1.10 \text{ V}$ ) was allowed to be completely discharged at 298 K. The relative concentration of  $\text{Zn}^{2+}$  to  $\text{Cu}^{2+}$ ,  $\left\{ \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \right\}$  is : [AIEEE 2007]  
 (A)  $9.65 \times 10^4$  (B) Antilog (24.08) (C) 37.3 (D)  $10^{37.3}$
48. Given the data at 25°C,  
 $\text{Ag}_{(s)} + \text{I}^{-}_{(aq)} \rightarrow \text{AgI}_{(s)} + \text{e}^{-}$ ,  $E^0 = 0.152 \text{ V}$   
 $\text{Ag}_{(s)} \rightarrow \text{Ag}^{+}_{(aq)} + \text{e}^{-}$ ,  $E^0 = -0.800 \text{ V}$   
 What is the value of  $\log K_{\text{sp}}$  for AgI ?  
 (Where  $K_{\text{sp}}$  = solubility product)  
 $\left( 2.303 \frac{RT}{F} = 0.059 \text{ V} \right)$  [AIEEE 2006]  
 (A) -8.12 (B) +8.612 (C) -37.83 (D) -16.13

## 5. SOME COMMERCIAL BATTERIES

Any battery or cell that we use as a source of electrical energy is basically an electrochemical cell where oxidising and reducing agents are made to react by using a suitable device. In principle, any redox reaction can be used as the basis of an electrochemical cell, but there are limitations to the use of most reactions as the basis of practical batteries. A battery should be reasonably light and compact and its voltage should not vary appreciably during the use.

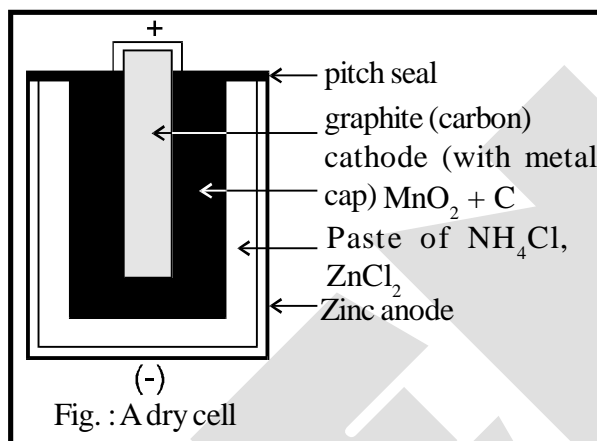
There are mainly two types of cells :

(i) primary cells and (ii) secondary cells. In primary cells, the reaction occurs only once and the battery then becomes dead over a period of time and cannot be used again. (For example, dry cell, mercury cell.) Contrary to this, secondary cells can be recharged by passing a current through them so that they can be used again and again. (For example, lead storage battery, nickel-cadmium storage cell.)

## 5.1 Primary Batteries

### 5.1.1 Dry cell or Leclanche cell :

The most familiar type of battery is the dry cell which is a compact of Leclanche cell known after its discoverer Leclanche (fig.) : In this cell, the anode consists of a zinc container and the cathode is a graphite rod surrounded by powdered  $\text{MnO}_2$  and carbon. The space between the electrodes is filled with a moist paste of  $\text{NH}_4\text{Cl}$  and  $\text{ZnCl}_2$ . The electrode reactions are complex, but they can be written approximately as follows.



- **Anode**  $\text{Zn(s)} \longrightarrow \text{Zn}^{+2} + 2\text{e}^-$
- **Cathode**  $\text{MnO}_2 + \text{NH}_4^+ + \text{e}^- \longrightarrow \text{MnO(OH)} + \text{NH}_3$

In the cathode reaction, manganese is reduced from the +4 oxidation state to the +3 state. Ammonia is not liberated as a gas but combines with  $\text{Zn}^{2+}$  to form  $\text{Zn}(\text{NH}_3)_4^{2+}$  ion. The cell has a potential of nearly 1.5 V.

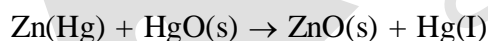
### 5.1.2 Mercury cell :

Mercury cell, suitable for low current devices like hearing aids, watches, etc. consists of zinc & mercury amalgam as anode and a paste of  $\text{HgO}$  and carbon as the cathode. The electrolyte is a paste of  $\text{KOH}$  and  $\text{ZnO}$ . The electrode reactions for the cell are given below:

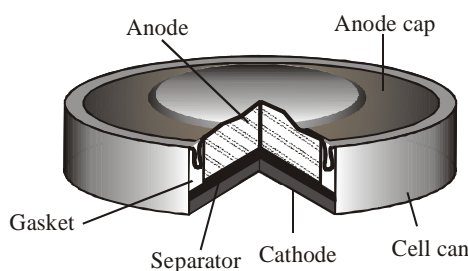
**Anode :**  $\text{Zn(Hg)} + 2\text{OH}^- \rightarrow \text{ZnO(s)} + \text{H}_2\text{O} + 2\text{e}^-$

**Cathode :**  $\text{HgO} + 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Hg(I)} + 2\text{OH}^-$

The overall reaction is represented by



The cell potential is approximately 1.35 V and remains constant during its life as the overall reaction does not involve any ion in solution whose concentration can change during its life time.



Commonly used mercury cell.  
The reducing agent is zinc and  
the oxidising agent is mercury  
(II) oxide.

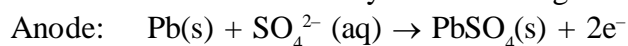
## 5.2 Secondary Batteries

A secondary cell after use can be recharged by passing current through it in the opposite direction so that it can be used again. A good secondary cell can undergo a large number of discharging and charging cycles.

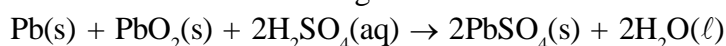
### 5.2.1 Lead storage cell :

The most important secondary cell is the lead storage battery commonly used in automobiles and invertors. It consists of a lead anode and a grid of lead packed with lead dioxide ( $\text{PbO}_2$ ) as cathode. A 38% solution of sulphuric acid is used as an electrolyte.

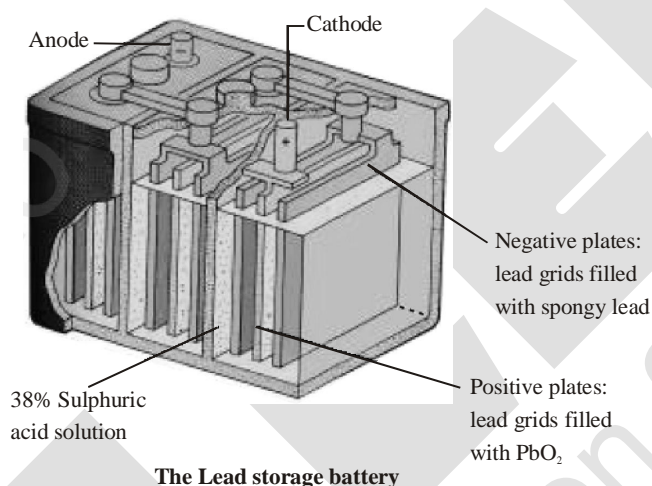
The cell reactions when the battery is in use are given below:



i.e., overall cell reaction consisting of cathode and anode reactions is:

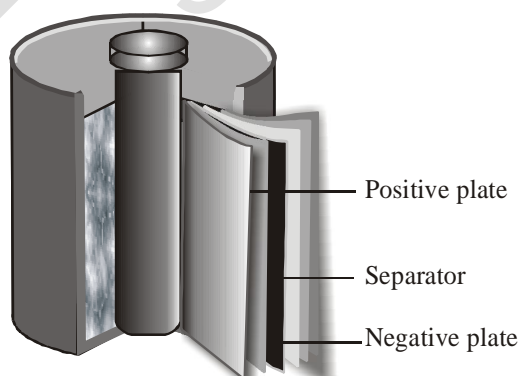


On charging the battery the reaction is reversed and  $\text{PbSO}_4(\text{s})$  on anode and cathode is converted into Pb and  $\text{PbO}_2$ , respectively



### 5.2.2 Nickel-cadmium cell :

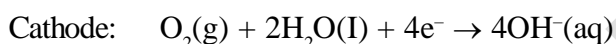
Another important secondary cell is the nickel-cadmium cell which has longer life than the lead storage cell but more expensive to manufacture. We shall not go into details of working of the cell and the electrode reactions during charging and discharging. The overall reaction during discharge is:



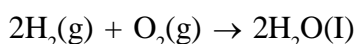
A rechargeable nickel-cadmium cell in a jelly roll arrangement and separated by a layer soaked in moist sodium or potassium hydroxide

## 5.3 FUEL CELLS

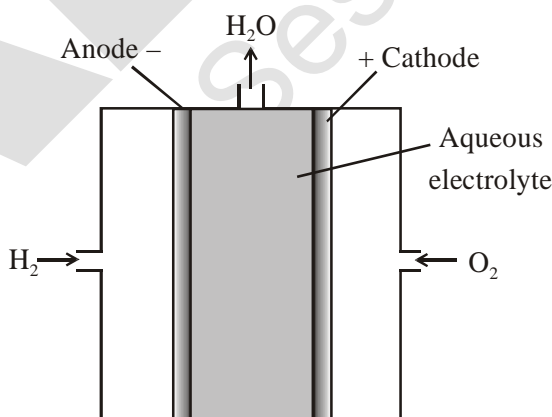
Production of electricity by thermal plants is not a very efficient method and is a major source of pollution. In such plants, the chemical energy (heat of combustion) of fossil fuels (coal, gas or oil) is first used for converting water into high pressure steam. This is then used to run a turbine to produce electricity. We know that a galvanic cell directly converts chemical energy into electricity and is highly efficient. It is now possible to make such cells in which reactants are fed continuously to the electrodes and products are removed continuously from the electrolyte compartment. Galvanic cells that are designed to convert the energy of combustion of fuels like hydrogen, methane, methanol, etc. directly into electrical energy are called fuel cells. One of the most successful fuel cells uses the reaction of hydrogen with oxygen to form water. The cell was used for providing electrical power in the Apollo space programme. The water vapours produced during the reaction were condensed and added to the drinking water supply for the astronauts. In the cell, hydrogen and oxygen are bubbled through porous carbon electrodes into concentrated aqueous sodium hydroxide solution. Catalysts like finely divided platinum or palladium metal are incorporated into the electrodes for increasing the rate of electrode reactions. The electrode reactions are given below:



Overall reaction being:



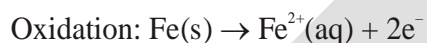
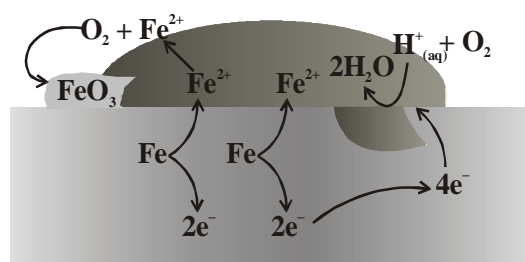
The cell runs continuously as long as the reactions are supplied. Fuel cells produce electricity with an efficiency of about 70% compared to thermal plants whose efficiency is about 40%. There has been tremendous progress in the development of new electrode materials, better catalysts and electrolytes for increasing the efficiency of fuel cells. These have been used in automobiles on an experimental basis. Fuel cells are pollution free and in view of their future importance, a variety of fuel cells have been fabricated and tried.



Fuel cell using  $\text{H}_2$  and  $\text{O}_2$  produces electricity

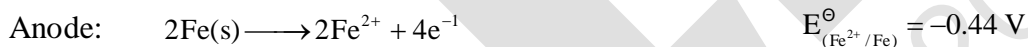
## 6. CORROSION :

Corrosion slowly coats the surfaces of metallic objects with oxides or other salts of the metal. The rusting of iron, tarnishing of silver, development of green coating on copper and bronze are some of the examples of corrosion. It causes enormous damage to buildings, bridges, ships and to all objects made of metals especially that of iron. We lose crores of rupees every year on account of corrosion. In corrosion, a metal is oxidised by loss of electrons to oxygen and formation of oxides. Corrosion of iron (commonly known as rusting) occurs in presence of water and air. The chemistry of corrosion is quite complex but it may be considered essentially as an electrochemical phenomenon. At a particular spot of an object made of iron, oxidation takes place and that spot behaves as anode and we can write the reaction

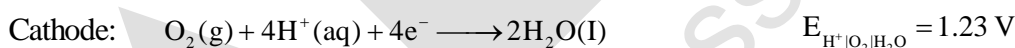


Atmospheric

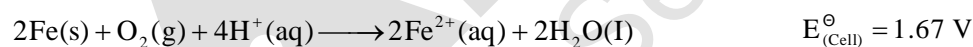
### Corrosion of iron in atmosphere



Electrons released at anodic spot move through the metal and go to another spot on the metal and reduce oxygen in presence of  $\text{H}^{+}$  (which is believed to be available from  $\text{H}_2\text{CO}_3$  formed due to dissolution of carbon dioxide from air into water. Hydrogen ion in water may also be available due to dissolution of other acidic oxides from the atmosphere). This spot behaves as cathode with the reaction



The overall reaction being:

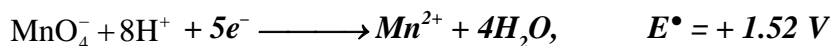


The ferrous ions are further oxidised by atmospheric oxygen to ferric ions which come out as rust in the form of hydrated ferric oxide ( $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ ) and with further production of hydrogen ions.

Prevention of corrosion is of prime importance. It not only saves money but also helps in preventing accidents such as a bridge collapse or failure of a key component due to corrosion. One of the simplest methods of preventing corrosion is to prevent the surface of the metallic object to come in contact with atmosphere. This can be done by covering the surface with paint or by some chemicals (e.g. bisphenol). Another simple method is to cover the surface by other metals (Sn, Zn, etc.) that are inert or react to save the object. An electrochemical method is to provide a sacrificial electrode of another metal (like Mg, Zn, etc.). Which corrodes itself but saves the object.



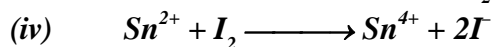
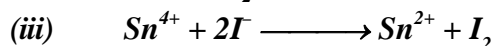
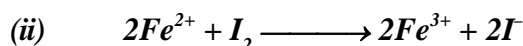
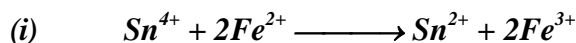
Ex.1  $E^\circ$  of some oxidants are given as :



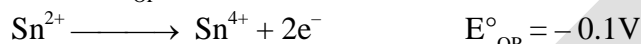
(a) Select the strongest reductant and oxidant in these.

(b) Select the weakest reductant and oxidant in these.

(c) Select the spontaneous reaction from the changes given below.



Sol. (a) More the  $E^\circ_{OP}$ , more is the tendency for oxidation. Therefore, since maximum  $E^\circ_{OP}$  stands for :



$\therefore$  Strongest reductant :  $Sn^{2+}$

and weakest oxidant :  $Sn^{4+}$

(b) More +ve is  $E^\circ_{RP}$ , more is the tendency for reduction. Therefore, since maximum  $E^\circ_{RP}$  stands for :



$\therefore$  Strongest oxidant :  $MnO_4^-$

and weakest reductant :  $Mn^{2+}$

**Note :-** Stronger is oxidant, weaker is its conjugate reductant and vice-versa.

(c) For (i)  $E^\circ_{Cell} = E^\circ_{OP_{Fe^{2+}/Fe^{3+}}} + E^\circ_{RP_{Sn^{4+}/Sn^{2+}}} = -0.77 + 0.1$

$Fe^{2+}$  oxidizes and  $Sn^{4+}$  reduces in change.

$$\therefore E^\circ_{Cell} = E^\circ_{OP_{Fe^{2+}/Fe^{3+}}} + E^\circ_{RP_{Sn^{4+}/Sn^{2+}}} = -0.77 + 0.1 = -0.67 \text{ V}$$

$E^\circ_{Cell}$  is negative.

$\therefore$  (i) Is non-spontaneous change.

For (ii)  $E^\circ_{Cell} = E^\circ_{OP_{Fe^{2+}/Fe^{3+}}} + E^\circ_{RP_{I_2/I^-}} = -0.77 + 0.54 = -0.23 \text{ V}$

$\therefore$  (ii) reaction is non-spontaneous change.

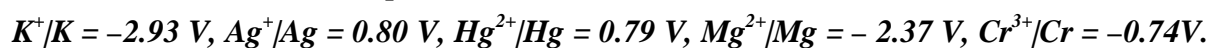
For (iii)  $E^\circ_{Cell} = E^\circ_{OP_{I^-/I_2}} + E^\circ_{RP_{Sn^{4+}/Sn^{2+}}} = -0.54 + 0.1 = -0.44 \text{ V}$

$\therefore$  (iii) Reaction is non-spontaneous change.

For (iv)  $E^\circ_{Cell} = E^\circ_{OP_{Sn^{2+}/Sn^{4+}}} + E^\circ_{RP_{I_2/I^-}} = -0.1 + 0.54 = +0.44 \text{ V}$

(iv) Reaction is spontaneous change.

**Ex.1** Given the standard electrode potentials ;



Arrange these metals in their increasing order of reducing power.

**Sol.** More is  $E^\circ_{RP}$ , more is the tendency to get reduced or more is the oxidising power or lesser is reducing power.  $Ag < Hg < Cr < Mg < K$

**Ex.2** A cell is prepared by dipping a copper rod in 1 M  $CuSO_4$  solution and a nickel rod in 1M  $NiSO_4$ . The standard reduction potentials of copper and nickel electrodes are + 0.34 V and -0.25 V respectively.

(i) Which electrode will work as anode and which as cathode ?

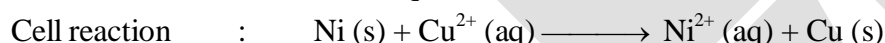
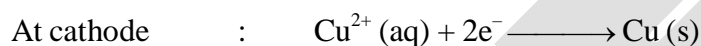
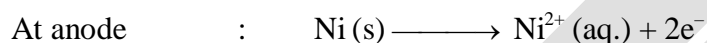
(ii) What will be the cell reaction ?

(iii) How is the cell represented ?

(iv) Calculate the EMF of the cell.

**Sol.** (i) The nickel electrode with smaller  $E^\circ$  value (-0.25 V) will work as anode while copper electrode with more  $E^\circ$  value (+0.34V) will work as cathode.

(ii) The cell reaction may be written as :

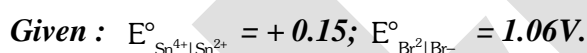


(iii) The cell may be represented as :



(iv)  $EMF \text{ of cell} = E^\circ_{cathode} - E^\circ_{anode} = (+0.34) - (-0.25) = 0.59 \text{ V}$

**Ex.4** Predict whether the following reaction can occur under standard conditions or not.



**Sol.**  $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 1.06 - 0.15 = 0.91 \text{ V}.$

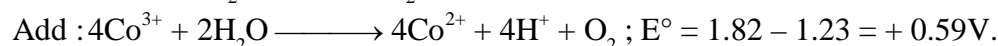
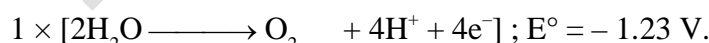
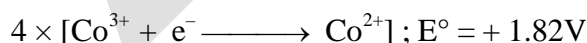
Since,  $E^\circ_{cell}$  comes out to be positive, this means that the reaction can occur.

**Ex.5** Given that,  $Co^{3+} + e^- \longrightarrow Co^{2+}$   $E^\circ = +1.82 \text{ V}$



Explain why  $Co^{3+}$  is not stable in aqueous solutions.

**Sol.** The  $E^\circ_{cell}$  can be calculated as follows :



Since,  $E^\circ_{cell}$  is positive, the cell reaction is spontaneous. This means that  $Co^{3+}$  ions will take part in the reaction. Therefore,  $Co^{3+}$  is not stable.

**Ex.6** The 0.1 M copper sulphate solution in which copper electrode is dipped at 25°C. Calculate the electrode reduction potential of copper electrode.

[Given :  $E_{\text{Cu}^{2+}|\text{Cu}}^0 = 0.34\text{V}$ ]

**Sol :**  $\text{Cu}^{+2} + 2\text{e}^- \rightarrow \text{Cu}$

$$E_{\text{red}} = E_{\text{red}}^0 - \frac{0.059}{n} \log Q = E_{\text{Cu}^{2+}|\text{Cu}}^0 - \frac{0.0591}{2} \log \frac{1}{[\text{Cu}^{2+}]}$$

$$\begin{aligned} \text{So } E &= 0.34 - \frac{0.0591}{2} \log 10 \\ &= 0.34 - 0.03 = 0.31 \text{ volts} \end{aligned}$$

**Ex.7** Calculate the EMF of the cell :  $\text{Cr}|\text{Cr}^{+3} (0.1\text{M}) || \text{Fe}^{+2} (0.01\text{M})|\text{Fe}$   
(Given :  $E_{\text{Cr}^{+3}|\text{Cr}}^0 = -0.75\text{V}$ ,  $E_{\text{Fe}^{+2}|\text{Fe}}^0 = -0.45\text{V}$ )

**Sol.** Half cell reactions are :

- **At anode :**  $[\text{Cr} \rightarrow \text{Cr}^{+3} + 3\text{e}^-] \times 2$
- **At cathode :**  $[\text{Fe}^{+2} + 2\text{e}^- \rightarrow \text{Fe}] \times 3$

Over all reaction :  $2\text{Cr(s)} + 3\text{Fe}^{+2}(\text{aq.}) \rightarrow 2\text{Cr}^{+3}(\text{aq.}) + 3\text{Fe(s.)}$

$$E_{\text{cell}}^0 = E_{\text{Cr}|\text{Cr}^{+3}}^0 + E_{\text{Fe}^{+2}|\text{Fe}}^0 = 0.75 + (-0.45) = 0.30\text{V}$$

$$E_{\text{cell}} = E^0 - \frac{0.0591}{n} \log Q = 0.30 - \frac{0.0591}{6} \log \frac{[\text{Cr}^{+3}]^2}{[\text{Fe}^{+2}]^3} = 0.30 - \frac{0.0591}{6} \log \frac{[0.1]^2}{[0.01]^3} = 0.26\text{V}$$

**Ex.8** The measured e.m.f. at 25°C for the cell reaction,  
 $\text{Zn(s)} + \text{Cu}^{2+}(\text{1.0M}) \longrightarrow \text{Cu(s)} + \text{Zn}^{2+}(\text{0.1M})$  is 1.3 volt, Calculate  $E^0$  for the cell reaction.

**Sol.** Using Nernst equation (at 298 K),  $E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}(\text{aq})]}{[\text{Cu}^{2+}(\text{aq})]}$

Here,  $E_{\text{cell}} = 1.3\text{V}$ ,  $[\text{Cu}^{2+}(\text{aq})] = 1.0\text{M}$ ,  $[\text{Zn}^{2+}(\text{aq})] = 0.1\text{M}$ ,  $E_{\text{cell}}^0 = ?$

Substituting the values,  $E_{\text{cell}}^0 = 1.27\text{V}$

**Ex.9** The emf of a cell corresponding to the reaction

$\text{Zn} + 2\text{H}^+(\text{aq}) \longrightarrow \text{Zn}^{2+}(\text{0.1M}) + \text{H}_2(\text{g})$  1 atm  
is 0.28 volt at 25°C. Calculate the pH of the solution at the hydrogen electrode.

$$E_{\text{Zn}^{2+}|\text{Zn}}^0 = -0.76 \text{ volt and } E_{\text{H}^+|\text{H}_2}^0 = 0$$

**Sol.**  $E_{\text{cell}}^0 = 0.76\text{ volt}$

$$\text{Applying Nernst equation, } E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}]\text{P}_{\text{H}_2}}{[\text{H}^+]^2}$$

$$0.28 = 0.76 - \frac{0.0591}{2} \log \frac{(0.1) \times 1}{[\text{H}^+]^2}, \text{ pH} = 8.62$$

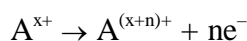
**Ex.10** The half cell oxidation potential of a half-cell  $A^{x+}, A^{(x+n)+} | Pt$  were found to be as follows :

|                   |       |       |
|-------------------|-------|-------|
| % of reduced form | 24.4  | 48.8  |
| Cell potential  V | 0.101 | 0.115 |

Determine the value of n.

$$[\text{take } \frac{2.303RT}{F} = 0.06, \log_{10} 24.4 = 1.387, \log_{10} 75.6 = 1.878, \log_{10} 48.8 = 1.688, \log_{10} 51.2 = 1.709]$$

**Sol.** The half-cell reaction is -



Its Nernst equation is -

$$E = E^{\circ} - 2.303 \frac{RT}{nF} \log \frac{[A^{(x+n)+}]}{[A^{x+}]} = E^{\circ} - \left( \frac{0.06V}{n} \right) \log \left( \frac{\text{oxidized form}}{\text{reduced form}} \right)$$

Substituting the given values, we get

$$0.101 \text{ V} = E^{\circ} - \left( \frac{0.06V}{n} \right) \log \frac{75.6}{24.4} = E^{\circ} - \left( \frac{0.06V}{n} \right) (0.491) \dots\dots(i)$$

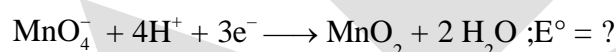
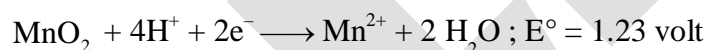
$$0.115 \text{ V} = E^{\circ} - \left( \frac{0.06V}{n} \right) \log \frac{51.2}{48.8} = E^{\circ} - \left( \frac{0.06V}{n} \right) (0.021) \dots\dots(ii)$$

$$\text{eq. (ii)} - \text{(i)}, n = 2$$

**Ex.11** What is the standard electrode potential for the electrode  $MnO_4^{-} / MnO_2$  in solution

$$E^{\circ}_{MnO_4^{-}/Mn^{2+}} = 1.51 \text{ volt}, E^{\circ}_{MnO_2/Mn^{2+}} = 1.23 \text{ volt}$$

**Sol.**  $MnO_4^{-} + 8H^{+} + 5e^{-} \longrightarrow Mn^{2+} + 4H_2O$  ;  $E^{\circ} = 1.51 \text{ volt}$



$$E^{\circ} = \frac{5 \times 1.51 - 2 \times 1.23}{3} = \frac{7.55 - 2.45}{3} = \frac{5.09}{3} = 1.70 \text{ volt}$$

**Ex.12** Calculate  $\Delta G^{\circ}$  for the reaction :  $Cu^{2+} (aq) + Fe (s) \rightleftharpoons Fe^{2+} (aq) + Cu (s)$  .

$$\text{Given that } E^{\circ}_{Cu^{2+}/Cu} = +0.34 \text{ V}, E^{\circ}_{Fe^{2+}/Fe} = -0.44 \text{ V}$$

**Sol.** The cell reactions are :

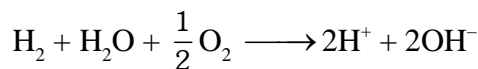


$$\text{We know that : } \Delta G^{\circ} = -nF E^{\circ}_{\text{cell}} ; n = 2$$

$$E^{\circ}_{\text{cell}} = [E^{\circ}_{(Cu^{2+}/Cu)} - E^{\circ}_{(Fe^{2+}/Fe)}] = (+0.34 \text{ V}) - (-0.44 \text{ V}) = +0.78 \text{ V and } F = 96500 \text{ C}$$

$$\therefore \Delta G^{\circ} = -nF E^{\circ}_{\text{cell}} = -(2) \times (96500 \text{ C}) \times (+0.78 \text{ V}) = -150540 \text{ CV} = -150540 \text{ J}$$

**Ex.13** At 298 K the standard free energy of formation of  $\text{H}_2\text{O}(l)$  is  $-256.5 \text{ kJ/mol}$  &  $\text{OH}^-$  is  $80 \text{ kJ/mol}$ . What will be emf at 298 K of the cell  $\text{H}_2(\text{g}, 1 \text{ bar}) | \text{H}^+(1\text{M}) || \text{OH}^-(1\text{M}) | \text{O}_2(\text{g}, 1 \text{ bar})$



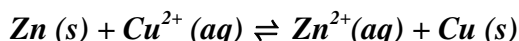
$$\Delta G^\circ = -256.5 + 2 \times 80 = -96.5 \text{ kJ}$$

$$-\Delta G^\circ = nFE^\circ$$

$$+ 96.5 \times 1000 = 2 \times 96500 \times E^\circ$$

$$E^\circ = 0.5 \text{ Volt}$$

**Ex.14** Calculate the equilibrium constant for the reaction at 298 K.



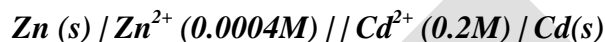
**Given**,  $E^\circ_{\text{Zn}^{2+}|\text{Zn}} = -0.76 \text{ V}$  and  $E^\circ_{\text{Cu}^{2+}|\text{Cu}} = +0.34 \text{ V}$

**Sol.** We know that,  $\log K_c = \frac{nE^\circ_{\text{cell}}}{0.0591}$

$$E^\circ_{\text{cell}} = [E^\circ_{\text{Cathode}} - E^\circ_{\text{Anode}}] = [(+0.34 \text{ V}) - (-0.76 \text{ V})] = 1.10 \text{ V}, n = 2,$$

$$\therefore \log K_c = \frac{2 \times (1.10 \text{ V})}{(0.0591 \text{ V})} = 37.29, K_c = \text{Antilog } 37.29 = 1.95 \times 10^{37}$$

**Ex.15** Calculate the cell e.m.f. and  $\Delta G$  for the cell reaction at 298 K for the cell.



**Given**,  $E^\circ_{\text{Zn}^{2+}|\text{Zn}} = -0.763 \text{ V}$ ;  $E^\circ_{\text{Cd}^{2+}|\text{Cd}} = -0.403 \text{ V}$  at 298 K.

$$F = 96500 \text{ C mol}^{-1}$$

**Sol.** **Step I.** Calculation of cell e.m.f. :

According to Nernst equation,

$$E = E^\circ - \frac{0.0591}{n} \log \frac{[\text{Zn}^{2+}(\text{aq})]}{[\text{Cd}^{2+}(\text{aq})]}$$

$$E^\circ_{\text{cell}} = E^\circ_{(\text{Cd}^{2+}/\text{Cd})} - E^\circ_{(\text{Zn}^{2+}/\text{Zn})} = (-0.403) - (-0.763) = 0.36 \text{ V}$$

$$[\text{Zn}^{2+}(\text{aq})] = 0.0004 \text{ M}, [\text{Cd}^{2+}(\text{aq})] = 0.2 \text{ M}, n = 2$$

$$E = (0.36) - \frac{(0.059 \text{ V})}{2} \log \frac{0.0004}{0.2} = 0.36 - \frac{(0.059 \text{ V})}{2} \times (-2.69990) = 0.36 \text{ V} + 0.08 = 0.44 \text{ V}$$

**Step II.** Calculation of  $\Delta G$  :

$$\Delta G = -nFE^\circ_{\text{cell}}$$

$$E^\circ_{\text{cell}} = 0.44 \text{ V}, n = 2 \text{ mol}, F = 96500 \text{ C mol}^{-1}$$

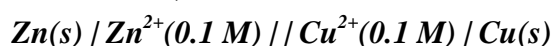
$$\therefore \Delta G = -(2 \text{ mol}) \times (96500 \text{ C mol}^{-1}) \times (0.44 \text{ V})$$

$$= -84920 \text{ CV} = -84920 \text{ J}$$

**Ex.16** The cell  $\text{Pt} / \text{H}_2(\text{g}) (1 \text{ atm}) / \text{H}^+ ; \text{pH} = x // \text{Normal calomal electrode}$  has EMF of 0.64 volt at  $25^\circ\text{C}$ . The standard reduction potential of normal calomal electrode is 0.28 V. What is the pH of solution in anodic compartment. Take  $\frac{2.303RT}{F} = 0.06$  at 298 K.

**Sol.**  $E_{\text{H}^+/\text{H}_2} = -0.06 \log \frac{1}{[\text{H}^+]} = -0.06 \text{pH}$   
 $\Rightarrow 0.64 = E_{\text{cathode}} - E_{\text{Anode}} = 0.28 - (-0.06 \text{pH})$   
 $\Rightarrow \text{pH} = \frac{0.64 - 0.28}{0.06} = \frac{0.36}{0.06} = 6$

**Ex.17** Consider a Galvanic cell,



by what factor, the electrolyte in anodic half cell should be diluted to increase the emf by 9 milli volt at 298 K.

**Ans.**  $E = E^\circ_{\text{cell}} - \frac{0.06}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$   
 $E_1 = E^\circ_{\text{cell}} - 0.03 \log \frac{(0.1)}{(0.1)}$   
 $E_2 = E^\circ_{\text{cell}} - 0.03 \log \frac{(0.1/x)}{(0.1)}$  {x is the factor by which electrolyte is diluted.}  
 $E_2 - E_1 = 9 \times 10^{-3} = 0 - 0.03 \log \left( \frac{1}{x} \right)$   
 $0.009 = 0.03 \log X$   
 $\frac{9 \times 10^{-3}}{3 \times 10^{-2}} = 0.3 = \log X$   
 $X = 2$

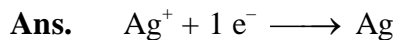
**Ex.18** A disposable galvanic cell  $\text{Zn} | \text{Zn}^{2+} || \text{Sn}^{2+} | \text{Sn}$  is produced using 1.0 mL of 0.5 M  $\text{Zn}(\text{NO}_3)_2$  and 1.0 mL of 0.50 M  $\text{Sn}(\text{NO}_3)_2$ . It is needed to power a pace-maker that draws a constant current of  $10^{-6}$  Amp to run it and requires atleast 0.50 V to function. Calculate the value of  $[\text{Zn}^{2+}]$  when cell reaches 0.5 V at 298 K.

(Given :  $E^\circ (\text{Zn}^{2+}/\text{Zn}) = -0.76\text{V}$ ;  $E^\circ (\text{Sn}^{2+}/\text{Sn}) = -0.14 \text{ V}$ ).

**Ans.** 1  
 $E = 0.5 \text{ V} = 0.62 - \frac{0.059}{2} \log \frac{0.5+x}{0.5-x}$   
 $\therefore \text{Zn} + \text{Sn}^{2+}_{0.5-x} \rightleftharpoons \text{Sn} + \text{Zn}^{2+}_{0.5+x}$   
 $\Rightarrow \log \frac{0.5+x}{0.5-x} = \frac{0.12 \times 2}{0.0592} \approx 4$   
 $\Rightarrow \frac{0.5+x}{0.5-x} = 10^4$   
 or  $x \approx 0.5 \text{ M}$   
 $\therefore [\text{Zn}^{2+}] = 1.0 \text{ M}$

**Ex.19** An alloy of Pb-Ag weighing 54 mg was dissolved in desired amount of  $\text{HNO}_3$  & volume was made upto 500ml. An Ag electrode was dipped in solution and then connected to standard hydrogen electrode anode. Then calculate % of Ag in alloy.

**Given :**  $E_{\text{cell}} = 0.5 \text{ V}$ ;  $E_{\text{Ag}^+/\text{Ag}}^\circ = 0.8 \text{ V}$   $\frac{2.303RT}{F} = 0.06$



$$E_{\text{cell}} = 0.5 = 0.8 + \frac{0.06}{1} \log [\text{Ag}^+]$$

$$\log [\text{Ag}^+] = \frac{-0.30}{0.06} = -5$$

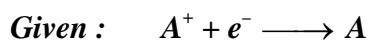
$$[\text{Ag}^+] = 10^{-5} \text{ mol/L}$$

$$\text{moles of Ag}^+ \text{ in } 500 \text{ ml} = \frac{10^{-5}}{2}$$

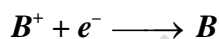
$$\text{Mass of Ag} = \frac{10^{-5}}{2} \times 108$$

$$\% \text{ Ag} = \frac{\frac{10^{-5}}{2} \times 108}{54 \times 10^{-3}} \times 100 = 1$$

**Ex.20.** A solution contains  $\text{A}^+$  and  $\text{B}^+$  in such a concentration that both deposit simultaneously. If current of 9.65 amp was passed through 100 ml solution for 55 seconds then find the final concentration of  $\text{A}^+$  ions if initial concentration of  $\text{B}^+$  is 0.1M.



$$E^\circ = -0.5 \text{ volt}$$



$$E^\circ = -0.56 \text{ volt}$$

$$\frac{2.303RT}{F} = 0.06$$

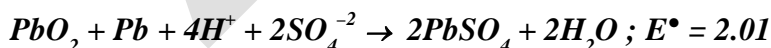
**Sol.**  $-0.5 - \frac{0.06}{1} \log \frac{1}{[\text{A}^+]} = -0.56 - \frac{0.06}{1} \log \frac{1}{[\text{B}^+]}$

$$0.06 = \frac{0.06}{1} \log \frac{[\text{B}^+]}{[\text{A}^+]}$$

$$\frac{[\text{B}^+]}{[\text{A}^+]} = 10$$

$$[\text{A}^+]_{\text{initial}} = 0.01 \text{ M}$$

**Ex.21** While the discharging of a lead storage battery following reaction take place.



Calculate the energy (in kJ) obtained from a lead storage battery in which 0.014 mol of lead is consumed. Assume a constant concentration of 10.M  $\text{H}_2\text{SO}_4$  ( $\log 2 = 0.3$ )

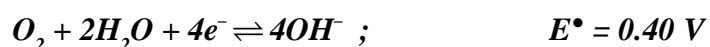
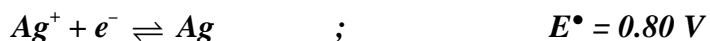
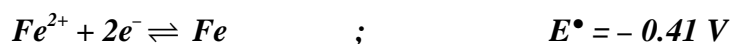
**Ans.**  $E = E^\circ - \frac{0.059}{n} \log \frac{1}{[\text{H}^+]^4 [\text{SO}_4^{2-}]^2} = 2.01 - \frac{0.059}{2} \log \frac{1}{[20]^4 [10]^2} = 2.22 \text{ V}$

$$\text{Energy} = qE$$

$$= 2 \times 0.014 \times 96500 \times 2.22$$

$$= 6000 \text{ J} = 6 \text{ kJ}$$

Ex.22 Consider the following standard reduction potentials :-



What would happen if a block of silver metal is connected to a buried iron pipe via a wire:-

(A) The silver metal would corrode, a current would be produced in the wire, and  $O_2$  would be reduced on the surface of the iron pipe.

(B) The silver metal would corrode, a current would be produced in the wire, and  $Fe^{2+}$  would be reduced on the surface of the iron pipe.

(C) The iron pipe would corrode, a current would be produced in the wire, and  $Ag^+$  would be reduced on the surface of the silver metal.

(D) The iron pipe would corrode, no current would be produced in the wire, and  $O_2$  would be reduced on the surface of the iron pipe.

Sol. (D)

## 7. ELECTROLYSIS :

The process of decomposition of an electrolyte by the passage of electricity is called **electrolysis** or electrolytic dissociation. It is carried out in electrolytic cell where electrical energy is converted into chemical energy. For electrolysis to take place two suitable electrodes are immersed in the liquid or solution of an electrolyte containing ions. When an electric potential is applied between the electrodes, the positively charged ions move towards the negative cathode and negatively ions move towards the positive anode, when a cation reaches the cathode, it takes up electron(s) and thus gets its charge neutralised. Thus the gain of electrons (decrease in oxidation number) means reduction takes place at the cathode.

Similarly when an anion it reaches the anode, gives up electron(s) and thus gets discharged. Loss of electrons (Increase in oxidation number) means oxidation takes place at anode.

- The tendency of an electrode to lose electrons is known as the **oxidation potential**.
- The tendency of an electrode to gain electrons is known as the **reduction potential**.
- **Greater oxidation potential means stronger is tendency to get oxidised and act as a reducing agent or reductant.**
- **Greater reduction potential means stronger is tendency to get reduced and act as an oxidising agent (oxidant).**

### (a) Electrolysis of fused sodium chloride :

When fused sodium chloride is electrolysed,  $Na^+$  ions moves towards the cathode and  $Cl^-$  ions moves towards the anode. At cathode  $Na^+$  ions accept electrons to form sodium metal. At anode each  $Cl^-$  ion loses an electron to form  $Cl_2$  gas.

- **At anode :**  $Cl^- \longrightarrow \frac{1}{2} Cl_2 + e^- ; E_{OP}^0 = -1.36V$
- **At cathode :**  $Na^+ + e^- \longrightarrow Na(s) ; E_{RP}^0 = -2.71V$



**(b) Electrolysis of aqueous solution of KBr**

The solution of KBr contain  $K^+$ ,  $Br^-$  & small amounts of  $H^+$ ,  $OH^-$  (due to small dissociation of water)

- **At anode :**  $2Br^-(aq.) \longrightarrow Br_2(g) + 2e^-$
- **At cathode :**  $2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$
- If more than one types of ions are present at a given electrode, then the one ion is the liberated which requires least energy. The energy required to liberate an ion is provided by the applied potential between electrodes. This potential is called **discharge or deposition potential**.

**Note :**

1. In aqueous solution most electropositive metal cations for eg. (s-block &  $Al^{3+}$ ) will not discharge at cathode instead  $H_2O$  is reduced.  $2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$
2. In aqueous solution cations of moderately electropositive metals (Mn, Co, Fe, Zn etc.) and least electropositive metals (Cu, Hg, Au, Ag, Pt) get discharged at cathode first.
3. **Active vs Inactive electrodes :**
  - Sometimes the metal electrodes in the cell are active and the metals themselves are components of the half reactions or influence the reaction of electrode.
  - For many redox reactions, however, there are no reactants or products capable of serving as electrodes. Inactive electrodes are used, most commonly rods of graphite or platinum, materials that conduct electrons into or out of the cell but cannot take part in the half-reactions.
  - Platinum is used  $\because$  highly conducting, unreactive.  
highly malleable and ductile.

**❖ Examples of Electrolysis :**

- **Electrolysis of aq.  $PbBr_2$**  (Using inert (Pt|graphite) electrodes).  
**Cathode :**  $Pb^{2+} + 2e^- \rightarrow Pb(s)$   $E^0 = 0.126V$   
**Anode :**  $2Br^- \rightarrow Br_2 + 2e^-$   $E^0 = -1.08 V$   
 $E_{cell} = -0.126 - (0.108) \times 10 = -1.206 V$   
 $E_{ext} > 1.206 V$
- **Electrolysis of aq.  $CuSO_4$**  (Using inert (Pt|graphite) electrodes).  
**Cathode :**  $Cu^{2+} + 2e^- \rightarrow Cu(s)$   $E^0 = 0.34 V$   
 $2e^- + 2H_2O(l) \rightarrow H_2(g) + 2OH^-(aq)$   $E^0 = -0.83V$   
**Anode :**  $2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^-$   $E^0 = -2.05 V$   
 $2H_2O(l) \rightarrow O_2 + 4H^+ + 4e^-$   $E^0 = -1.23 V$   
 $\therefore$  Cu discharged at cathode and  $O_2$  at anode.
- **Electrolysis of aq.  $NaCl$**  (Using inert (Pt|graphite) electrodes).  
**Cathode :**  $Na^+ + e^- \rightarrow Na$   $E^0 = -2.71 V$   
 $2e^- + 2H_2O(l) \rightarrow H_2(g) + 2OH^-$   $E^0 = -0.83 V$   
**Anode :**  $2Cl^- \rightarrow Cl_2 + 2e^-$   $E^0_{ox} = -1.30 V$   
 $2H_2O(l) \rightarrow O_2 + 4H^+ + 4e^-$   $E^0_{ox} = -1.23 V$

Rate of production of  $\text{Cl}_2$  is more than rate of production of  $\text{O}_2$  gas because of greater activation energy barrier for  $\text{O}_2$  production, therefore  $\text{Cl}_2$  is released at anode and  $\text{H}_2$  at cathode.

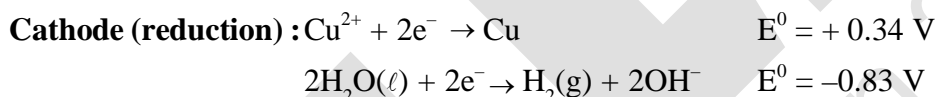
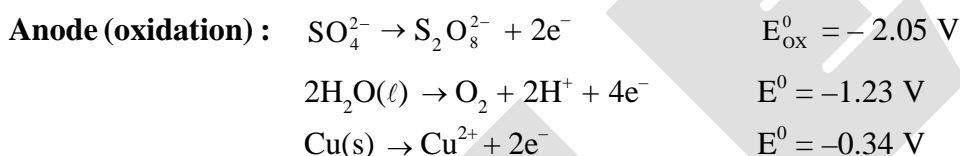
**Note:(i)** As observed from electrode potential values discharge potential for  $\text{O}_2$  is less than for  $\text{Cl}_2$ . According to thermodynamics, oxidation of  $\text{H}_2\text{O}$  to produce  $\text{O}_2$  should take place on anode but experimentally (experiment from chemical kinetics) the rate of oxidation of water is found to be very slow. To increase its rate, the greater potential difference has to be applied called over voltage or over potential.

Because of this oxidation of  $\text{Cl}^-$  ions also become feasible and this takes place at anode. Electrode potential values do not take into account such effects as : Activation energy of process or non-uniform ionic concentration in solution.

**(ii)** Electrode potentials are thermodynamic intensive properties obtained experimentally under ideal & standard conditions. Sometimes in working conditions additional potentials are required for discharging. This difference is termed as overvoltage or overpotential.

❖ **Electrolysis using attackable (reactive) electrodes :**

• **Electrolysis of aq.  $\text{CuSO}_4$  using Cu electrode.**



∴ Both oxidation and reduction of copper occurs and density of solution remains constant.

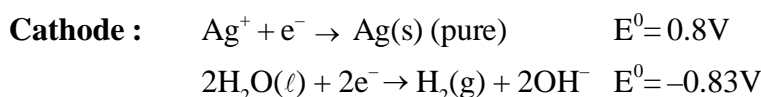
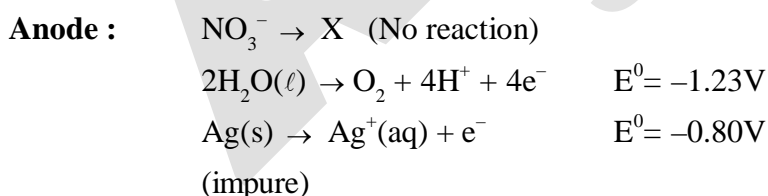
• **Electrolytic Refining**

**Electrolysis of  $\text{AgNO}_3$  (aq) using Ag cathode & Ag anode.**

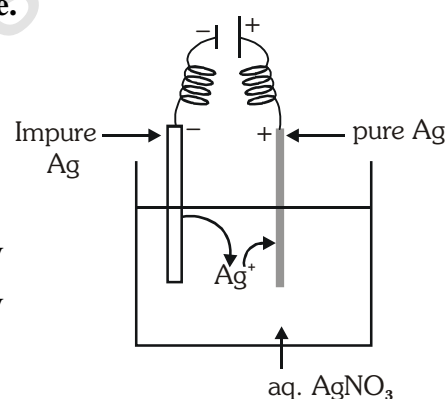
Impure metal → Anode ;

Pure Metal → Cathode ;

Metal salt solution → Electrolyte



∴ Both oxidation and reduction of Ag occurs and mass transfer of Ag occurs from anode (impure Ag) to cathode (pure Ag). Electrical energy provided by battery is used for mass transfer of Ag from anode to cathode.



## PRODUCTS OF ELECTROLYSIS OF SOME ELECTROLYTES

| S.No.  | Electrolyte                           | Electrode      | Product obtained at anode                          | Product obtained at cathode |
|--------|---------------------------------------|----------------|----------------------------------------------------|-----------------------------|
| (i)    | Fused NaCl(molten)                    | Pt or Graphite | Cl <sub>2</sub>                                    | Na                          |
| (ii)   | Aqueous NaCl(conc.)                   | Pt or Graphite | Cl <sub>2</sub>                                    | H <sub>2</sub>              |
| (iii)  | dil. NaCl                             | Pt or Graphite | O <sub>2</sub>                                     | H <sub>2</sub>              |
| (iv)   | Aqueous NaOH                          | Pt or Graphite | O <sub>2</sub>                                     | H <sub>2</sub>              |
| (v)    | Fused NaOH                            | Pt or Graphite | O <sub>2</sub>                                     | Na                          |
| (vi)   | Aqueous CuSO <sub>4</sub>             | Pt or Graphite | O <sub>2</sub>                                     | Cu                          |
| (vii)  | Dilute HCl                            | Pt or Graphite | Cl <sub>2</sub>                                    | H <sub>2</sub>              |
| (viii) | Dilute H <sub>2</sub> SO <sub>4</sub> | Pt or Graphite | O <sub>2</sub>                                     | H <sub>2</sub>              |
| (ix)   | Aqueous AgNO <sub>3</sub>             | Pt of Graphite | O <sub>2</sub>                                     | Ag                          |
| (x)    | Aqueous CH <sub>3</sub> COONa         | Pt of Graphite | CH <sub>3</sub> -CH <sub>3</sub> + CO <sub>2</sub> | H <sub>2</sub>              |

## 8. FARADAY'S LAWS OF ELECTROLYSIS :

Michael Faraday on basis of experiments deduced two important laws :

- (a) **Faraday's first law of electrolysis :** This law states that *"The amount of a substance deposited or discharged at an electrode is directly proportional to the charge passing through the electrolytic solution"*.

If a current of **I** amperes is passed for **t** seconds, (the quantity of charge **Q** in coulombs). If **W** gram of substances is deposited by **Q** coulombs of electricity, then

$$W \propto Q \propto i \times t$$

$$W = Z \times i \times t = \frac{E}{96500} \times i \times t = \eta \times \frac{E}{F} \times i \times t$$

$$\text{moles of } e^- = n_e = \frac{\eta \times i \times t}{F} = \text{no. of equivalents of species discharged During electrolysis :}$$

Where 1 Faraday (1F) is defined as charge of 1 mole electrons =  $eN_A = 1 F \cong 96500 \text{ C}$

**Hence faraday (F) is the quantity of charge in coulombs required to deposit one g equivalent of any substance.**

**E** = Equivalent mass of species discharged

$\eta$  = current efficiency in fraction if current efficiency is not mentioned, by default it is assumed to be 1 (100%).

**Z** is constant of proportionality and is known as **electrochemical equivalent**. Its value is different for different species, when  $Q = 1 \text{ coulomb}$ ,  $W = Z$ , thus electro chemical equivalent may be defined as the weight in grams of an element liberated by the passage of 1 coulomb of electricity.

Electrochemical equivalent of species (**Z**) =  $\frac{E}{96500} \text{ gm | coulomb.}$

- (b) **Faraday's second law :** This law states that the amounts of different substances deposited in different solutions connected in series at electrodes by passage of the same quantity of electricity are proportional to their equivalent masses(**E**).

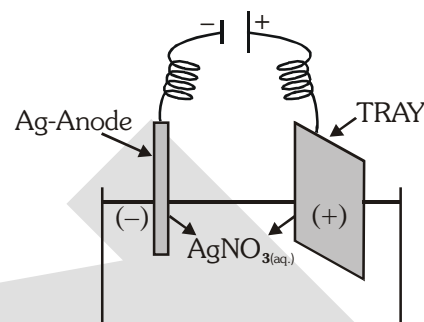
$$W \propto E \text{ (E = equivalent mass)}$$

If  $W_1$  and  $W_2$  be the amounts of two different substances deposited at electrodes and  $E_1$  and  $E_2$  be the equivalent weights respectively then -

$$\frac{W_1}{W_2} = \frac{E_1}{E_2}$$

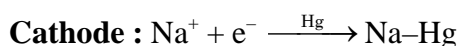
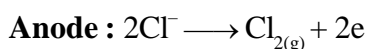
## 9. APPLICATION OF ELECTROLYSIS

- |      |                          |                                                                                              |
|------|--------------------------|----------------------------------------------------------------------------------------------|
| (i)  | <b>Electroplating :</b>  | Metal used for plating → ANODE<br>Object to be plated → CATHODE                              |
| (ii) | <b>Electrorefining :</b> | Impure metal → ANODE (see fig.)<br>Pure metal → CATHODE<br>Metal salt solution → electrolyte |



- (iii) **Electro-metallurgy** : (Electrolytic reduction)

**Ex. Electrolysis of NaCl (from seawater) Using Hg-cathode.**



## EXERCISE # III

49. Calculate the no. of electrons lost or gained during electrolysis of  
(a) 3.55 gm of  $\text{Cl}^-$  ions    (b) 1 gm  $\text{Cu}^{2+}$  ions    (c) 2.7 gm of  $\text{Al}^{3+}$  ions
50. How many faradays of electricity are involved in each of the case  
(a) 0.25 mole  $\text{Al}^{3+}$  is converted to Al.  
(b) 27.6 gm of  $\text{SO}_3$  is converted to  $\text{SO}_3^{2-}$   
(c) The  $\text{Cu}^{2+}$  in 1100 ml of 0.5 M  $\text{Cu}^{2+}$  is converted to Cu.
51. 0.5 mole of electron is passed through two electrolytic cells in series. One contains silver ions, and the other zinc ions. Assume that only cathode reaction in each cell is the reduction of the ion to the metal. How many gm of each metals will be deposited.
52. If 0.224 litre of  $\text{H}_2$  gas is formed at the cathode, how much  $\text{O}_2$  gas is formed at the anode under identical conditions?
53. Chromium metal can be plated out from an acidic solution containing  $\text{CrO}_3$  according to following equation:  
$$\text{CrO}_3(\text{aq}) + 6\text{H}^+(\text{aq}) + 6\text{e}^- \rightarrow \text{Cr}(\text{s}) + 3\text{H}_2\text{O}$$
  
Calculate :  
(i) How many grams of chromium will be plated out by 24125 coulombs and  
(ii) How long will it take to plate out 1.5 gm of chromium by using 12.5 ampere current
54. Which of the substances Na, Hg, S, Pt and graphite can be used as electrodes in electrolytic cells having aqueous solution ?  
(A) Hg and Pt    (B) Hg, Pt and graphite  
(C) Na, S    (D) Na, Hg, S

55. The products formed when an aqueous solution of NaBr is electrolyzed in a cell having inert electrodes are :  
(A) Na and Br<sub>2</sub> (B) Na and O<sub>2</sub> (C) H<sub>2</sub>, Br<sub>2</sub> and NaOH (D) H<sub>2</sub> and O<sub>2</sub>
56. A solution of sodium sulphate in water is electrolysed using inert electrodes. The products at the cathode and anode are respectively.  
(A) H<sub>2</sub>, O<sub>2</sub> (B) O<sub>2</sub>, H<sub>2</sub> (C) O<sub>2</sub>, Na (D) none
57. When an aqueous solution of lithium chloride is electrolysed using graphite electrodes  
(A) Cl<sub>2</sub> is liberated at the anode.  
(B) Li is deposited at the cathode  
(C) as the current flows, pH of the solution remains constant  
(D) as the current flows, pH of the solution decreases.
58. The amount of an ion discharged during electrolysis is not directly proportional to :  
(A) resistance (B) time  
(C) current strength (D) electrochemical equivalent of the element
59. Number of electrons involved in the electrodeposition of 63.5 g of Cu from a solution of CuSO<sub>4</sub> is : ( $N_A = 6 \times 10^{23}$ )  
(A)  $6 \times 10^{23}$  (B)  $3 \times 10^{23}$  (C)  $12 \times 10^{23}$  (D)  $6 \times 10^{22}$
60. When one coulomb of electricity is passed through an electrolytic solution the mass deposited on the electrode is equal to :  
(A) equivalent weight (B) molecular weight  
(C) electrochemical equivalent (D) one gram
61. Electro chemical equivalent of a substance is 0.0006; its e wt. is :  
(A) 57.9 (B) 28.95  
(C) 115.8 (D) cannot be calculated
62. W g of copper deposited in a copper voltameter when an electric current of 2 ampere is passed for 2 hours. If one ampere of electric current is passed for 4 hours in the same voltameter, copper deposited will be :  
(A) W (B) W/2 (C) W/4 (D) 2W
63. When the same electric current is passed through the solution of different electrolytes in series the amounts of elements deposited on the electrodes are in the ratio of their:  
(A) atomic number (B) atomic masses (C) specific gravities (D) equivalent masses
64. The amount of electricity that can deposit 108 g. of silver from silver nitrate solution is:  
(A) 1 ampere (B) 1 coulomb  
(C) 1 Faraday (D) 2 ampere
65. The ratio of weights of hydrogen and magnesium deposited by the same amount of electricity from aqueous H<sub>2</sub>SO<sub>4</sub> and fused MgSO<sub>4</sub> are :  
(A) 1 : 8 (B) 1 : 12 (C) 1 : 16 (D) None of these
66. A current of 9.65 amp. flowing for 10 minute deposits 3.0 g of a metal. The equivalent wt. of the metal is :  
(A) 10 (B) 30 (C) 50 (D) 96.5

67. 1 mole of Al is deposited by X coulomb of electricity passing through aluminium nitrate solution. The number of moles of silver deposited by X coulomb of electricity from silver nitrate solution is  
(A) 3 (B) 4 (C) 2 (D) 1
68. When an electric current is passed through acid diluted water, 112 ml. of hydrogen gas at STP collects at the cathode in 965 second. The current passed, in ampere is :  
(A) 1.0 (B) 0.5 (C) 0.1 (D) 2.0
69. A factory produces 40 kg. of calcium in two hours by electrolysis. How much aluminium can be produced by the same current in two hours :—  
(At wt. of Ca = 40, Al = 27)  
(A) 22 kg. (B) 18 kg. (C) 9 kg. (D) 27 kg.
70. Calculate the volume of hydrogen at STP obtained by passing a current of 0.536 ampere through acidified water for 30 minutes.  
(A) 0.135 litre (B) 0.227 litre (C) 0.057 litre (D) 0.454 litre
71. An electric current is passed through silver voltameter connected to a water voltameter in series. The cathode of the silver voltameter weighed 0.108g more at the end of the electrolysis. The volume of oxygen evolved at STP is :  
(A) 56.75 cm<sup>3</sup> (B) 567.5 cm<sup>3</sup> (C) 5.675 cm<sup>3</sup> (D) 113.5 cm<sup>3</sup>
72. When, during electrolysis of a solution of AgNO<sub>3</sub>, 9650 coulombs of charge pass through the electroplating bath, the mass of silver deposited on the cathode will be : [AIEEE 2003]  
(A) 21.6g (B) 108g (C) 1.08g (D) 10.8g
73. Aluminium oxide may be electrolysed at 1000°C to furnish aluminium metal ( 1 Faraday = 96500 Coulombs). The cathode reaction is [AIEEE 2005]  
 $\text{Al}^{3+} + 3\text{e}^- \longrightarrow \text{Al}$   
To prepare 5.12 kg of aluminium metal by this method would require,  
(A)  $5.49 \times 10^4$  C of electric charge (B)  $5.49 \times 10^1$  C of electric charge  
(C)  $5.49 \times 10^7$  C of electric charge (D)  $1.83 \times 10^7$  C of electric charge

**Ex.23** How much charge is present on 1 mole of  $\text{Cu}^{+2}$  ion in faraday. (1 Faraday = 96500 coulomb)

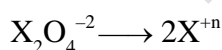
**Ans.** 1 mole  $\text{e}^- = 1 \text{ mol proton} = 1\text{F}$

**2 Faraday**

**Ex.24** For an element 'X' the process of oxidation is :  $\text{X}_2\text{O}_4^{-2} \longrightarrow \text{product}$

If 965 A current when passed for 100 seconds for 0.1 mol of  $\text{X}_2\text{O}_4^{-2}$ , find oxidation state of X in new compound ?

**Ans.** +3



$\therefore$  oxidation process  $3 < n$ , N-factor =  $2(n - 3)$

$$\text{so } 0.1 \times 2(n-3) = \frac{i \times t}{96500} = \frac{965 \times 100}{96500}$$

$$2(n-3) = 10, n - 3 = 5, n = 8$$

**Ex.25** How many litres of chlorine at 1 atm & 273K will be deposited by 100 amp. current flowing for 5 hours through molten NaCl?

**Sol :**  $Q = It = 100 \times 5 \times 60 \times 60 = 18 \times 10^5 \text{ C}$

$$W = ZQ = \frac{E}{96500} \times 18 \times 10^5 = \frac{18E}{96500} \times 10^5 = 662.2 \text{ g}, \left( E_{\text{Cl}_2} \frac{71}{2} = 35.5 \right)$$

$\therefore$  Volume of 71 g  $\text{Cl}_2$  at 1 atm & 273K = 22.4 L

$\therefore$  Volume of 662.2 g  $\text{Cl}_2$  at NTP =  $\frac{22.4}{71} \times 662.2 = 208.9 \text{ L}$

**Ex.26** How much time is required for complete decomposition of two moles of water at anode using 4 amperes current ?

**Sol.**  $\text{H}_2\text{O}(l) \longrightarrow \text{H}_2(g) + \frac{1}{2}\text{O}_2(g)$

For  $\text{H}_2$  :  $2 \times 2 = \frac{4 \times t}{96500} \Rightarrow t = 96500 \text{ sec}$ ,

**Ex.27** How much charge (in F) must flow through solution during electrolysis of aq.  $\text{Na}_2\text{SO}_4$  at  $0^\circ\text{C}$  and 1 atm to produce 33.6 L of product gases at 50% current efficiency ?

**Ans.**  $\text{H}_2\text{O} \xrightarrow{2F} \text{H}_2 + \frac{1}{2}\text{O}_2$

$$V \quad V/2 \Rightarrow \frac{3}{2}V = 33.6 \text{ L} \Rightarrow V = 22.4 \text{ L}$$

$$Q \times \frac{50}{100} = 2F \Rightarrow Q = 4F$$

**Ex.28** Calculate the time required to coat a metal surface of  $80 \text{ cm}^2$  with 0.005 mm thick layer of silver (density =  $10.5 \text{ g cm}^{-3}$ ) with the passage of 3A current through silver nitrate solution.

**Sol.**  $\therefore$  Volume of layer of silver =  $0.005 \times 10^{-1} \times 80 = 0.04 \text{ cm}^3$

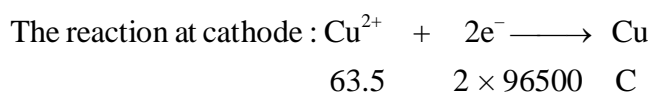
$\therefore$  Mass = Density  $\times$  volume =  $10.5 \times 0.04 = 0.42 \text{ g}$

$$\text{So } w = \frac{E}{96500} \times It \Rightarrow 0.42 = \frac{108}{96500} \times 3 \times t$$

$$t = \frac{0.42 \times 96500}{108 \times 3} = 125.09 \text{ seconds.}$$

**Ex.29** A Solution of copper (II) sulphate is electrolysed between copper electrodes by a current of 10.0 amperes passing for one hour. What changes occur at the electrodes and in the solution?

**Sol.** According to Faraday's first law of electrolysis :



The quantity of charge passed =  $I \times t = (10 \text{ amp}) \times (60 \times 60 \text{ s}) = 36000 \text{ C}$ .

$2 \times 96500 \text{ C}$  of charge deposit copper - 63.5 g

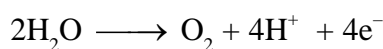
$$36500 \text{ C of charge deposit copper} = \frac{(63.5 \text{ g})}{(2 \times 96500 \text{ C})} \times (36000 \text{ C}) = 11.84 \text{ g}$$

Thus, 11.84 g of copper will dissolve from the anode and the same amount from the solution will get deposited on the cathode. The concentration of the solution will remain unchanged.

**Ex.30** An aqueous solution of  $\text{Na}_2\text{SO}_4$  was electrolysed for 10 min. 82 ml of a gas was produced at anode and collected over water at  $27^\circ\text{C}$  at a total pressure of 580 torr. Determine the current that was used in amp. , Given : Vapour pressure of  $\text{H}_2\text{O}$  at  $27^\circ\text{C} = 10 \text{ torr}$ ,  $R = 0.082 \text{ atm L/mol-K}$

**Ans** (1.6A)

At anode reaction will be



$\text{V}_{\text{O}_2}$  collected = 82 ml

$$\text{By PV} = nRT \quad \frac{(580 - 10)}{760} \times \frac{82}{1000} = (n_{\text{O}_2}) \times 0.0821 \times 300, \quad n_{\text{O}_2} = \frac{1}{400}$$

$$\text{By Faraday law} \quad \frac{W}{E} = \frac{i \times t}{96500}$$

$$\left(\frac{W}{M}\right) \times n = \frac{i \times t}{96500}, \quad \left(\frac{1}{400} \times 4\right) = \frac{i \times 10 \times 60}{96500}, \quad i = 1.6 \text{ A}$$

**Ex.31** The same current if passed through solution of silver nitrate and cupric salt connected in series. If the weight of silver deposited is 1.08 g. calculate the weight of copper deposited.

**Sol.** According to faradays second law

$$\frac{W_1}{W_2} = \frac{E_1}{E_2} \Rightarrow \frac{1.08}{W_2} = \frac{108}{31.75} \Rightarrow W_2 = 0.3175 \text{ g}$$

## 10 ELECTROLYTIC CONDUCTANCE

### 10.1 Resistance (R) :

Metallic and electrolytic conductors obey ohm's law according to which the resistance of a conductor is the ratio of the applied potential difference (V) to the current following(I).

$$R = \frac{V}{I}$$

• R is expressed in ohms.

- In the case of solution of electrolytes, the resistance offered by the solution to the flow of current is –

(a) Directly proportional to the distance between the electrodes

$$R \propto \ell$$

(b) Inversely proportional to the area of cross section of the electrodes

$$R \propto \frac{1}{A}$$



**10.2 Conductance or resistivity (G) :**

The conductance of a conductor is equal to reciprocal of resistance.

$$G = \frac{1}{R} \quad \bullet \text{ G is expressed in mho or } \Omega^{-1} \text{ or Siemen(S).}$$

$$[1\text{S} = 1\text{W}^{-1} \text{ S.I. unit}]$$

**10.3 Specific resistance or conductivity ( $\rho$ ) :**

The resistance (R) of a conductor of uniform cross section is directly proportional to its length( $\ell$ ) and inversely proportional to its area of cross section (A).

$$R \propto \frac{\ell}{A} \quad R = \rho \frac{\ell}{A}$$

where  $\rho$  is a constant and called resistivity or specific resistance.

When  $\ell = 1$ ,  $A = 1$ , then  $\rho = R$  thus the specific resistance may be defined as the resistance of a conductor of unit length and unit area of cross section.

- Unit of  $\rho \rightarrow \text{ohm.cm}$

**10.4 Specific conductance ( $\kappa$ ) :**

It is defined as the reciprocal of specific resistance

$$\kappa = \frac{1}{\rho},$$

$$G = \kappa / G^*, \quad G^* = \frac{l}{a} = \text{cell constant}$$

If  $\ell = 1 \text{ cm}$  &  $A = 1 \text{ cm}^2$  then  $\kappa = G$

Hence conductivity or specific conductance (F) of a solution is defined as the conductance of one centimeter cube of the solution of the electrolyte.

- Cell constant is a fixed quantity for a particular cell and is defined as the distance between two parallel electrodes of a cell divided by the area of cross section of the electrodes.

$$\kappa = G \times \text{cell constant}$$

- Unit of  $\kappa \rightarrow \text{ohm}^{-1} \text{ cm}^{-1}$
- SI unit of  $\kappa \rightarrow \text{S m}^{-1}$
- $1 \text{ S m}^{-1} = 100 \text{ ohm}^{-1} \text{ cm}^{-1}$

**10.5 Molar conductance ( $\lambda_m$  or  $\Lambda_m$ ) :** It is defined as the product of specific conductance ( $\kappa$ ) and the volume (V in mL) in which contains one mole of the electrolyte.

$$\Lambda_m = \kappa \times V \quad \text{and} \quad \Lambda_m = \frac{\kappa \times 1000}{M} \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1} \quad [\text{SI unit : S m}^2 \text{ mol}^{-1}]$$

- It can also be defined as conductance of 1 mole electrolyte completely dissolved between two plates separated by unit distance.

**10.6 Equivalent conductance ( $\lambda_{eq}$  or  $\Lambda_{eq}$ ) :** It is defined as the product of specific conductance ( $\kappa$ ) and the volume (V in mL) in which contains one equivalent of the electrolyte.

$$\Lambda_m = \kappa \times v \quad \text{and} \quad \Lambda_m = \frac{\kappa \times 1000}{M} \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1} \quad [\text{SI unit : S m}^2 \text{ eq}^{-1}]$$

- It can also be defined as conductance of 1 equivalent electrolyte completely dissolved between two plates separated by unit distance.

- Relation between  $\Lambda_{eq}$  and  $\Lambda_m$  :**

$$\Lambda_m = \frac{\kappa \times 1000}{M} \quad \text{and} \quad \Lambda_{eq} = \frac{\kappa \times 1000}{N}$$

We know that, **Normality = Valency Factor  $\times$  Molarity**

$$\text{or} \quad N = n \times M \Rightarrow \lambda_{eq} = \frac{\lambda_m}{n}$$

#  $n$  = total cationic (or anionic) charge of salt.

$$\text{Ex.} \quad \Lambda_{eq} [\text{Al}_2(\text{SO}_4)_3] = \frac{\Lambda_m [\text{Al}_2(\text{SO}_4)_3]}{6}, \quad L_{eq \text{ NaCl}} = \frac{\Lambda_m \text{ NaCl}}{1}, \quad L_{eq \text{ CaCl}_2} = \frac{\Lambda_m \text{ CaCl}_2}{2}$$

## 11 EFFECT OF DILUTION ON THE CONDUCTIVITY OF ELECTROLYTES

- The degree of ionisation of weak electrolytes increases with the increase of dilution of the solution the conductivity is increases due to increasing the number of ions.
  - Effect of dilution on specific conductance :  
Specific conductance decreases with the increase of dilution of the solution due to the presence of no. of ions in 1 cm<sup>3</sup> solution decreases conductance also decrease on dilution.
  - Effect of dilution on equivalent|molar conductivity :  
The equivalent|molar conductivity increases with dilution. For strong electrolyte  $\lambda_m$  or  $\lambda_{eq}$  increases very slowly but for weak electrolytes  $\lambda_m$  &  $\lambda_{eq}$  increase sharply on dilution.
- When the whole of the electrolyte has ionised, further addition of the water brings a small change in the value of equivalent|molar conductance. This stage is called **infinite dilution**.
  - The ratio of equivalent conductivity at any dilution to equivalent conductivity at infinite dilution is called **conductivity ratio** or degree of dissociation of solute -

$$\alpha = \frac{\lambda_{eq.}}{\lambda_m^\infty} = \frac{\lambda_m}{\lambda_m^\infty}$$

[  $\lambda_m^\infty$  = molar conductance at  $\infty$  dilution.]

### ❖ Variation of conductivity and molar conductivity with concentration :

- Conductance and conductivity always decreases with the decrease in concentration both for weak and strong electrolytes.
- It is because the number of ions per unit volume that carry the current in a solution decreases on dilution decreasing I, C and K.

## ❖ Strong Electrolytes :

- For strong electrolytes,  $\Lambda$  increases slowly with dilution and can be represented by the equation

$$\Lambda = \Lambda^\circ - A C^{1/2}, A = \text{constant}$$

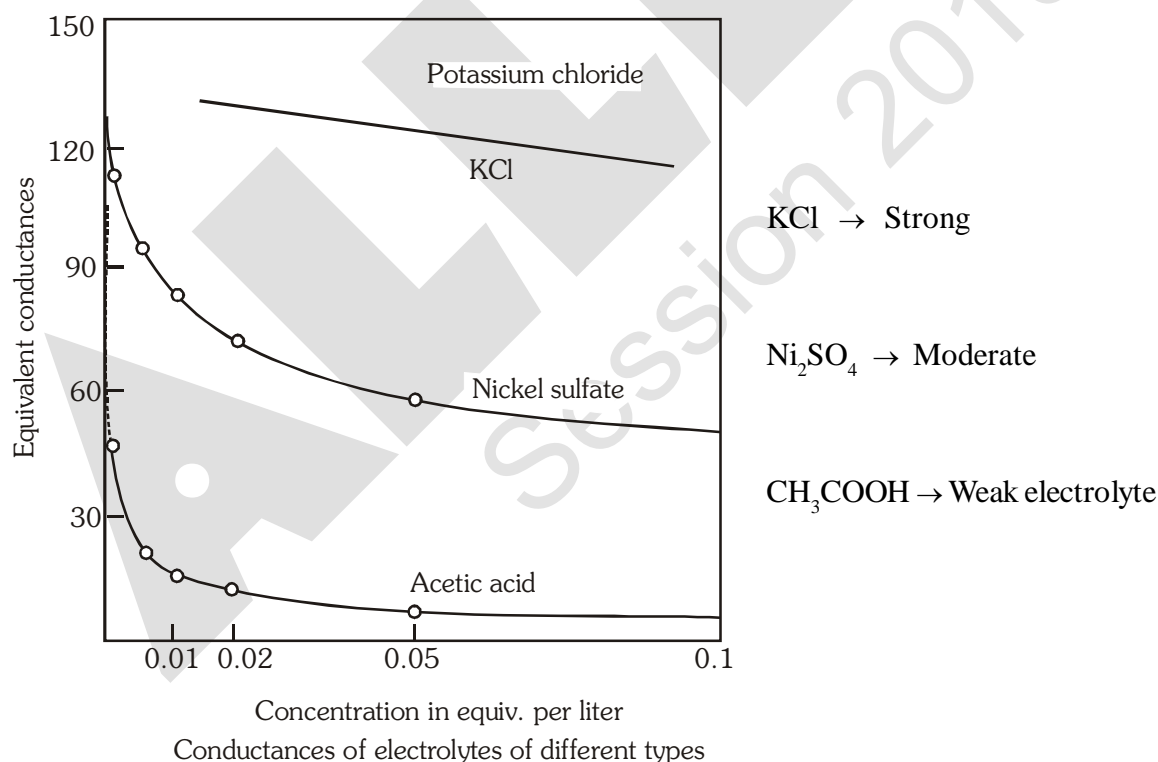
On dilution interionic separation increases causing free movement & less hindrance. This increases  $\Lambda_m$  &  $\Lambda_{eq.}$ .

For strong electrolytes  $\Lambda^\circ$  or  $\Lambda^\infty$  can be calculated graphically from y-intercept.

It can be seen that if we plot  $\Lambda_m$  against  $c^{1/2}$ , we obtain a straight line with intercept equal to  $\Lambda_m^\circ$  and slope equal to  $-A$ . The value of the constant  $A$  for a given solvent and temperature depends on the type of the electrolyte i.e., the charges on the cation and anion produced on the dissociation of the electrolyte in the solution. Thus,  $\text{NaCl}$ ,  $\text{CaCl}_2$ ,  $\text{MgSO}_4$  are known as 1 – 1, 2 – 1 and 2 – 2 electrolytes respectively. All electrolytes of a particular type have the same value for  $A$ .

## ❖ Weak electrolytes :

- Weak electrolytes like acetic acid have lower degree of dissociation at higher concentration and hence for such electrolytes, the change in  $\Lambda$  with dilution is due to increase in the number of ions solution containing a given amount of electrolyte.



- Note :** (A) Weaker the electrolyte more sharp will be increase of  $\Lambda_m$  or  $\Lambda_{eq}$  on dilution.  
 (B) same plot is also observed for  $\Lambda_m$  vs. molarity of respective electrolytes.

## 12. KOHLRAUSCH'S LAW

- "At infinite dilution, when dissociation is complete, each ion makes a definite contribution towards equivalent conductance of the electrolyte irrespective of the nature of the ion with which it is associated and the value of equivalent conductance at infinite dilution for any electrolyte is the sum of contribution of its constituent ions."

i.e., for  $A_{n+} B_{n-}$

$$\Lambda_{eq}^{\infty} = \Lambda_{eq}^{\infty}(+) + \Lambda_{eq}^{\infty}(-)$$

$$\Lambda_m^{\infty} = v_+ \Lambda_m^{\infty}(+) + v_- \Lambda_m^{\infty}(-)$$

$v_+$  = no. of cation in one formula unit of electrolyte.

$v_-$  = no. of anions in one formula unit of electrolyte.

**Note :**  $\lambda^{\infty} = \lambda^{\circ}$

$$\lambda_{eq+}^{\circ} = \frac{\lambda_m^{\circ}}{\text{charge on the cation}}$$

$$\lambda_{eq}^{\circ} \cdot Al^{3+} = \frac{\lambda_m^{\circ} Al^{3+}}{3}$$

$$\lambda_{eq}^{\circ} = \frac{\lambda_m^{\circ}}{\text{charge on the anion}}$$

$$\lambda_{eq}^{\circ}, \text{ electrolyte} = \frac{\lambda_m^{\circ} \text{ electrolyte}}{\text{total +ve charge on cations in electrolyte}}$$

or

$$\text{total -ve charge on anions in electrolyte}$$

**The Independent Migration of Ions.** A survey of equivalent conductances at infinite dilution of a number of electrolytes having an ion in common will bring to light certain regularities ;

### COMPARISON OF EQUIVALENT CONDUCTANCES AT INFINITE DILUTION

| Electrolyte                    | $\Lambda_0$ | Electrolyte                     | $\Lambda_0$ | Difference |
|--------------------------------|-------------|---------------------------------|-------------|------------|
| KCl                            | 130.0       | NaCl                            | 108.9       | 21.1       |
| KNO <sub>3</sub>               | 126.3       | NaNO <sub>3</sub>               | 105.2       | 21.1       |
| K <sub>2</sub> SO <sub>4</sub> | 133.0       | Na <sub>2</sub> SO <sub>4</sub> | 111.9       | 21.1       |

Observations of this kind were first made by **Kohlrausch (1879, 1885)** by comparing equivalent conductances at high dilutions; described them to the fact that under these conditions every ion makes a definite contribution towards the equivalent conductance of the electrolyte, irrespective of the nature of the other ion with which it is associated in the solution. The value of the equivalent conductance at infinite dilution may thus be regarded as made up of the sum of two independent factors, one characteristic of each ion; this result is known as Kohlrausch's law of independent migration of ions.

The ion conductance is a definite constant for each ion, in a given solvent, its value depending only on the temperature.

It will be seen later that the ion conductances at infinite dilution are related to the speeds with which the ions move under the influence of an applied potential gradient.

## ❖ Applications of Kohlrausch's law :

- Calculate  $\Lambda^\circ$  for any electrolyte from the  $\Lambda^\circ$  of individual ions.

An important use of ion conductances is to determine the equivalent conductance at infinite dilution of certain electrolytes which cannot be, or have not been, evaluated from experimental data. For example, with a weak electrolyte the extrapolation to infinite dilution is very uncertain, and with sparingly soluble salts the number of measurements which can be made at appreciably different concentrations is very limited. The value of  $\Lambda^\circ$  can, however, be obtained by adding the ion conductances. For example, the equivalent conductance of acetic acid at infinite dilution is the sum of the conductances of the hydrogen and acetate ions; the former is derived from a study of strong acids and the latter from measurements on acetates. It follows, therefore, that at  $25^\circ$ .

$$\Lambda^\circ_{(\text{CH}_3\text{CO}_2\text{H})} = \lambda^\circ_{\text{H}^+} + \lambda^\circ_{\text{CH}_3\text{CO}_2^-} = 349.8 + 40.9 = 390.7 \text{ ohms}^{-1} \text{ cm}^2$$

The same result can be derived in another manner which is often convenient since it avoids the necessity of separating the conductance of an electrolyte into the contributions of its constituent ions. The equivalent conductance of any weak electrolyte MA at infinite dilution it follows, therefore, that  $\Lambda^\circ(\text{MA}) = \Lambda^\circ(\text{MCl}) + \Lambda^\circ(\text{NaA}) - \Lambda^\circ(\text{NaCl})$ , [MCl, NaA, NaCl are strong electrolytes] where  $\Lambda^\circ(\text{MCl})$ ,  $\Lambda^\circ(\text{NaA})$  and  $\Lambda^\circ(\text{NaCl})$  are the equivalent conductances at infinite dilution of the chloride of the metal M, i.e., MCl, of the sodium salt of the anion A, i.e., NaA, and of sodium chloride, respectively. Any convenient anion may be used instead of the chloride ion, and similarly the sodium ion may be replaced by another metallic cation or by the hydrogen ion. For example, if  $\text{M}^+$  is the hydrogen ion and  $\text{A}^-$  is the acetate ion, it follows that

$$\begin{aligned}\Lambda^\circ(\text{CH}_3\text{COOH}) &= \Lambda^\circ(\text{HCl}) + \Lambda^\circ(\text{CH}_3\text{COONa}) - \Lambda^\circ(\text{NaCl}) \\ &= 426.16 + 91.0 - 126.45 \\ &= 390.71 \text{ ohms}^{-1} \text{ cm}^2 \text{ at } 25^\circ.\end{aligned}$$

Similarly :

$$\Lambda_m^\circ[\text{BaSO}_4] = \Lambda_m^\circ[\text{BaCl}_2] + \Lambda_m^\circ[\text{Na}_2\text{SO}_4] - 2\Lambda_m^\circ[\text{NaCl}]$$

- Degree of dissociation :

$\therefore$  Degree of dissociation

$$\frac{\text{equivalent conductance at a given concentration}}{\text{equivalent conductance at infinite dilution}}$$

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^\circ} = \frac{\Lambda_{eq}^c}{\Lambda_{eq}^\circ}$$

- Dissociation constant of weak electrolyte :

$$K_c = \frac{C\alpha^2}{1-\alpha} = \frac{C\left(\frac{\Lambda_m^c}{\Lambda_m^\circ}\right)^2}{1 - \frac{\Lambda_m^c}{\Lambda_m^\circ}}$$

- **Solubility(s) and  $K_{sp}$  of any sparingly soluble salt.**

Sparingly soluble salt = Very small solubility

Solubility = molarity  $\cong S \rightarrow 0$

So, solution can be considered to be of zero conc or infinite dilution.

$$\Lambda_m^s \cong \Lambda_m^s = \kappa = \frac{1000}{s}$$

$$s = \frac{\kappa \times 1000}{\Lambda_m^0}$$

### EXERCISE # IV

- The resistance of a conductivity cell filled with 0.01N solution of NaCl is 200 ohm at 18°C. Calculate the equivalent conductivity of the solution. The cell constant of the conductivity cell is 0.88 cm<sup>-1</sup>.
- The molar conductivity of 0.1 M CH<sub>3</sub>COOH solution is 4 S cm<sup>2</sup> mole<sup>-1</sup>. What is the specific conductivity and resistivity of the solution?
- The conductivity of pure water in a conductivity cell with electrodes of cross sectional area 4 cm<sup>2</sup> and 2 cm apart is 8 × 10<sup>-7</sup> S cm<sup>-1</sup>.
  - What is resistance of conductivity cell?
  - What current would flow through the cell under an applied potential difference of 1 volt?
- For 0.01N KCl, the resistivity 800 ohm cm. Calculate the conductivity and equivalent conductance.
- Equivalent conductance of 0.01 N Na<sub>2</sub>SO<sub>4</sub> solution is 120 ohm<sup>-1</sup> cm<sup>2</sup> eq<sup>-1</sup>. The equivalent conductance at infinite dilution is 150 ohm<sup>-1</sup> cm<sup>2</sup> eq<sup>-1</sup>. What is the degree of dissociation in 0.01 N Na<sub>2</sub>SO<sub>4</sub> solution?
- Saturated solution of AgCl at 25°C has specific conductance of 1.12 × 10<sup>-6</sup> ohm<sup>-1</sup> cm<sup>-1</sup>. The  $\lambda_{\infty}(\text{Ag}^+)$  and  $\lambda_{\infty}(\text{Cl}^-)$  are 54 and 58 ohm<sup>-1</sup> cm<sup>2</sup> | equi. respectively. Calculate the solubility product of AgCl at 25°C.
- The value of  $\Lambda_m^{\infty}$  for HCl, NaCl and CH<sub>3</sub>CO<sub>2</sub>Na are 425, 125 and 100 S cm<sup>2</sup> mol<sup>-1</sup> respectively. Calculate the value of  $\Lambda_m^{\infty}$  for acetic acid. If the equivalent conductivity of the given acetic acid is 48 at 25° C, calculate its degree of dissociation.
- For the strong electrolytes NaOH, NaCl and BaCl<sub>2</sub> the molar ionic conductivities at infinite dilution are 240 × 10<sup>-4</sup>, 125 × 10<sup>-4</sup> and 280.0 × 10<sup>-4</sup> mho cm<sup>2</sup> mol<sup>-1</sup> respectively. Calculate the molar conductivity of Ba(OH)<sub>2</sub> at infinite dilution.
- Electrolytic conduction differs from metallic conduction from the fact that in the former
  - The resistance increases with increasing temperature
  - The resistance decreases with increasing temperature
  - The resistance remains constant with increasing temperature
  - The resistance is independent of the length of the conductor
- Which of the following solution of KCl has the lowest value of specific conductance :
 

|         |           |            |             |
|---------|-----------|------------|-------------|
| (A) 1 M | (B) 0.1 M | (C) 0.01 M | (D) 0.001 M |
|---------|-----------|------------|-------------|

84. Which of the following solutions of KCl has the lowest value of equivalent conductance ?  
 (A) 1 M (B) 0.1 M (C) .01 M (D) .001 M
85. The molar conductance at infinite dilution of  $\text{AgNO}_3$ ,  $\text{AgCl}$  and  $\text{NaCl}$  are 115, 120 and 110 respectively. The molar conductance of  $\text{NaNO}_3$  is :—  
 (A) 110 (B) 105 (C) 130 (D) 150
86. The equivalent conductivity of 0.1 N  $\text{CH}_3\text{COOH}$  at 25 °C is 80 and at infinite dilution 400. The degree of dissociation of  $\text{CH}_3\text{COOH}$  is :  
 (A) 1 (B) 0.2 (C) 0.1 (D) 0.5
87. The specific conductance of a 0.01 M solution of KCl is  $0.0014 \text{ ohm}^{-1} \text{ cm}^{-1}$  at 25° C. Its equivalent conductance ( $\text{cm}^2 \text{ ohm}^{-1} \text{ equiv}^{-1}$ ) is :—  
 (A) 140 (B) 14 (C) 1.4 (D) 0.14
88. The resistance of 0.01 N solution of an electrolyte was found to be 200 ohm at 298 K using a conductivity cell of cell constant  $1.5 \text{ cm}^{-1}$ . The equivalent conductance of solution is :—  
 (A)  $750 \text{ mho cm}^2 \text{ eq}^{-1}$  (B)  $75 \text{ mho cm}^2 \text{ eq}^{-1}$   
 (C)  $750 \text{ mho}^{-1} \text{ cm}^2 \text{ eq}^{-1}$  (D)  $75 \text{ mho}^{-1} \text{ cm}^2 \text{ eq}^{-1}$
89. The resistance of 0.1 N solution of a acetic acid is 250 ohm. When measured in a cell of cell constant  $1.15 \text{ cm}^{-1}$ . The equivalent conductance (in  $\text{ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$ ) of 0.1 N acetic acid is  
 (A) 46 (B) 9.2 (C) 18.4 (D) 0.023
90. If 0.01 M solution of an electrolyte has a resistance of 40 ohms in a cell having a cell constant of  $0.4 \text{ cm}^{-1}$  then its molar conductance in  $\text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  is :  
 (A) 10 (B)  $10^2$  (C)  $10^3$  (D)  $10^4$
91. The conductivity of a saturated solution of  $\text{BaSO}_4$  is  $3.06 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$  and its molar conductance is  $1.53 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . The  $K_{sp}$  of  $\text{BaSO}_4$  will be :  
 (A)  $2 \times 10^{-4}$  (B)  $4 \times 10^{-4}$  (C)  $4 \times 10^{-3}$  (D)  $4 \times 10^{-6}$
92. The limiting molar conductivities  $\Lambda^0$  for  $\text{NaCl}$ ,  $\text{KBr}$  and  $\text{KCl}$  are 126, 152 and  $150 \text{ S cm}^2 \text{ mol}^{-1}$  respectively. The  $\Lambda_m^0$  for  $\text{NaBr}$  is : [AIEEE 2004]  
 (A)  $278 \text{ S cm}^2 \text{ mol}^{-1}$  (B)  $176 \text{ S cm}^2 \text{ mol}^{-1}$  (C)  $128 \text{ S cm}^2 \text{ mol}^{-1}$  (D)  $302 \text{ S cm}^2 \text{ mol}^{-1}$
93. Electrolyte  $\Lambda^\infty (\text{S cm}^2 \text{ mol}^{-1})$   
 $\text{KCl}$  149.9  
 $\text{KNO}_3$  145.0  
 $\text{HCl}$  426.2  
 $\text{NaOAc}$  91.0  
 $\text{NaCl}$  126.5  
 Calculate  $\Lambda_{\text{HOAc}}^\infty$  using appropriate molar conductances of the electrolytes listed above at infinite dilution in  $\text{H}_2\text{O}$  at 25°C [AIEEE 2005]  
 (A) 390.7 (B) 217.5 (C) 517.2 (D) 552.7
94. The highest electrical conductivity of the following aqueous solution is of [AIEEE 2005]  
 (A) 0.1 M fluoroacetic acid (B) 0.1 M difluoroacetic acid  
 (C) 0.1 M acetic acid (D) 0.1 M chloroacetic acid

95. The molar conductivities,  $\Lambda_{\text{NaOAc}}^0$  and  $\Lambda_{\text{HCl}}^0$  at infinite dilution in water at 25°C are 91.0 and 426.2 S cm<sup>2</sup>/mol respectively. To calculate  $\Lambda_{\text{HOAc}}^0$  the additional value required is :
- (A) KCl (B) NaOH (C) NaCl (D) H<sub>2</sub>O [AIEEE 2006]
96. Resistance of a conductivity cell filled with a solution of an electrolyte of concentration 0.1M is 100Ω. The conductivity of this solution is 1.29 Sm<sup>-1</sup>. Resistance of the same cell when filled with 0.02M of the same solution is 520Ω. The molar conductivity of 0.02M solution of the electrolyte will be.
- (A)  $124 \times 10^{-4} \text{ Sm}^2 \text{ mol}^{-1}$  (B)  $1240 \times 10^{-4} \text{ Sm}^2 \text{ mol}^{-1}$  [AIEEE 2006]  
(C)  $1.24 \times 10^4 \text{ Sm}^2 \text{ mol}^{-1}$  (D)  $12.4 \times 10^{-4} \text{ Sm}^2 \text{ mol}^{-1}$

❖ **Abnormal ion conductances of H<sup>+</sup> and OH<sup>-</sup> :**

It is supposed, as already indicated, that the hydrogen ion in water is H<sub>3</sub>O<sup>+</sup> with three hydrogen atoms attached to the central oxygen atom. When a potential gradient is applied to an aqueous solution containing hydrogen ions, the latter travel to some extent by the same mechanism as do other ions, but there is in addition another mechanism which permits of a more rapid ionic movement. This second process is believed to involve the transfer of a proton (H<sup>+</sup>) from a H<sub>3</sub>O<sup>+</sup> ion to an adjacent water molecule; thus



The resulting H<sub>3</sub>O<sup>+</sup> ion can now transfer a proton to another water molecule, and in this way the positive charge will be transferred a considerable distance in a short time. The electrical conductance will thus be much greater than that due solely to the normal mechanism.

**13. CONDUCTOMETRIC TITRATION :**

The principle of conductometric titration is based on the fact that during the titration, one of the ions is replaced by the other and invariably these two ions differ in the ionic conductivity with the result that conductivity of the solution varies during the course of titration. The equivalence point may be located graphically by plotting the change in conductance as a function of the volume of titrant added. In order to reduce the influence of errors in the conductometric titration to a minimum, the angle between the two branches of the titration curve should be as small as possible (see Fig. 6.2). If the angle is very obtuse, a small error in the conductance data can cause a large deviation. The following approximate rules will be found

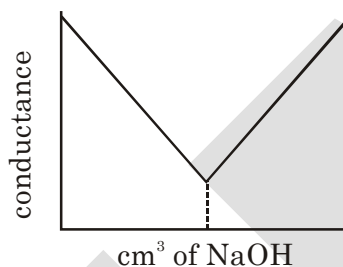
- The smaller the conductivity of the ion which replaces the reacting ion, the more accurate will be the result. Thus it is preferable to titrate a silver salt with lithium chloride rather than with HCl. Generally, cations should be titrated with lithium salts and anions with acetates as these ions have low conductivity.
- The larger the conductivity of the anion of the reagent which reacts with the cation to be determined, or vice versa, the more acute is the angle of titration curve.
- The titration of a slightly ionized salt does not give good results, since the conductivity increases continuously from the commencement. Hence, the salt present in the cell should be virtually completely dissociated; for a similar reason; the added reagent should also be as strong electrolyte. The main advantages to the conductometric titration are its applicability to very dilute, and coloured solutions and to systems that involve relative incomplete reactions. For example, which neither a potentiometric, nor indicator method can be used for the neutralization titration of phenol ( $K_a \times 10^{-10}$ ) a conductometric endpoint can be successfully applied.



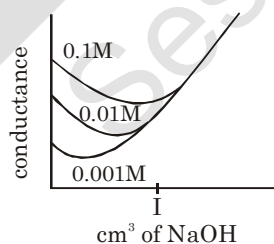
| Cation                                                       | $\text{H}_3\text{O}^+$ | $\text{NH}_4^+$ | $\text{K}^+$  | $\text{Na}^+$   | $\text{Ag}^+$             | $\text{Ca}^{2+}$   | $\text{Mg}^{2+}$ |
|--------------------------------------------------------------|------------------------|-----------------|---------------|-----------------|---------------------------|--------------------|------------------|
| $\lambda_m^\infty / (\Omega^{-1}\text{cm}^2\text{mol}^{-1})$ | 350.0                  | 73.5            | 73.5          | 50.1            | 62.1                      | 118.0              | 106.1            |
| Anion                                                        | $\text{OH}^-$          | $\text{Br}^-$   | $\text{Cl}^-$ | $\text{NO}_3^-$ | $\text{CH}_3\text{COO}^-$ | $\text{SO}_4^{2-}$ |                  |
| $\lambda_m^\infty / (\Omega^{-1}\text{cm}^2\text{mol}^{-1})$ | 199.2                  | 78.1            | 76.5          | 71.4            | 40.0                      | 159.6              |                  |

### Some Typical Conductometric Titration Curves are :

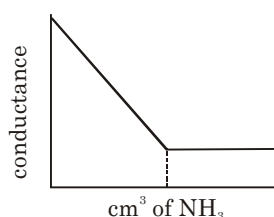
**13.1** Before NaOH is added, the conductance is high due to the presence of highly mobile hydrogen ions. When the base is added, the conductance falls due to the replacement of hydrogen ions by the added cation as  $\text{H}^+$  ions react with  $\text{OH}^-$  ions to form undissociated water. This decrease in the conductance continues till the equivalence point. At the equivalence point, the solution contains only NaCl. After the equivalence point, the conductance increases due to the large.



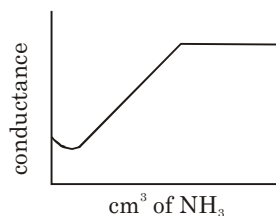
**13.2 Weak Acid with a Strong Base, e.g. acetic acid with NaOH:** Initially the conductance is low due to the feeble ionization of acetic acid. On the addition of base, there is decrease in conductance not only due to the replacement of  $\text{H}^+$  by  $\text{Na}^+$  but also suppresses the dissociation of acetic acid due to common ion acetate. But very soon, the conductance increases on adding NaOH as NaOH neutralizes the un-dissociated  $\text{CH}_3\text{COOH}$  to  $\text{CH}_3\text{COONa}$  which is the strong electrolyte. This increase in conductance continues up to the equivalence point. The graph near the equivalence point is curved due to the hydrolysis of salt  $\text{CH}_3\text{COONa}$ . Beyond the equivalence point, conductance increases more rapidly with the addition of NaOH due to the highly conducting  $\text{OH}^-$  ions.



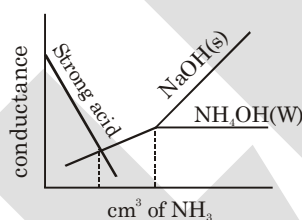
**13.3 Strong Acid with a Weak Base, e.g. sulphuric acid with dilute ammonia :** Initially the conductance is high and then it decreases due to the replacement of  $\text{H}^+$ . But after the endpoint has been reached the graph becomes almost horizontal, since the excess aqueous ammonia is not appreciably ionised in the presence of ammonium sulphate.



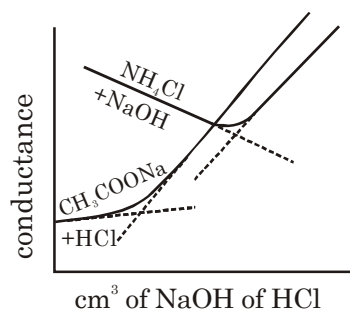
**13.4. Weak Acid with a Weak Base :** The nature of curve before the equivalence point is similar to the curve obtained by titrating weak acid against strong base. After the equivalence point, conductance virtually remains same as the weak base which is being added is feebly ionized and, therefore, is not much conducting



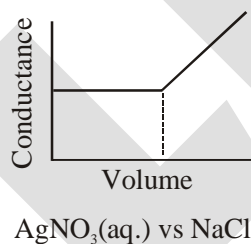
Mixture of a Strong Acid and a Weak Acid vs. a Strong Base or a Weak Base : In this curve there are two break points. The first break point corresponds to the neutralization of strong acid. When the strong acid has been completely neutralized only then the weak acid starts neutralizing. The second break point corresponds to the neutralization of weak acid and after that the conductance increases due to the excess of OH<sup>-</sup> ions in case of a strong base as the titrant. However, when the titrant is a weak base, it remains almost constant after the end point similar to



**Displacement (or Replacement) Titrations :** When a salt of a weak acid is titrated with a strong acid, the anion of the weak acid is replaced by that of the strong acid and weak acid itself is liberated in the undissociated form. Similarly, in the addition of a strong base to the salt of a weak base, the cation of the weak base is replaced by that of the stronger one and the weak base itself is generated in the undissociated form. If for example, M-HCl is added to 0.1 M solution of sodium acetate, the curve shown in Fig. 6.7 is obtained, the acetate ion is replaced by the chloride ion after the endpoint. The initial increase in conductivity is due to the fact that the conductivity of the chloride ion is slightly greater than that of acetate ion. Until the replacement is nearly complete, the solution contains enough sodium acetate to suppress the ionization of the liberated acetic acid, so resulting a negligible increase in the conductivity of the solution. However, near the equivalent point, the acetic acid is sufficiently ionized to affect the conductivity and a rounded portion of the curve is obtained. Beyond the equivalence point, when excess of HCl is present (ionization of acetic acid is very much suppressed) therefore, the conductivity arises rapidly. Care must be taken that to titrate a 0.1 M-salt of a weak acid, the dissociation constant should not be more than  $5 \times 10^{-4}$ , for a 0.01 M-salt solution,  $K_a < 5 \times 10^{-5}$  and for a 0.001 M-salt solution,  $K_a < 5 \times 10^{-6}$ , i.e., the ionization constant of the displacement acid or base divided by the original concentration of the salt must not exceed above  $5 \times 10^{-3}$ . Fig. 6.6. Also includes the titration of 0.01 M- ammonium chloride solution versus 0.1 M- sodium hydroxide solution. The decrease in conductivity during the displacement is caused by the displacement of ammonium ion of greater conductivity by sodium ion of smaller conductivity.



**13.5 Precipitation Titration and Complex Formation Titration :** A reaction may be made the basis of a conductometric precipitation titration provided the reaction product is sparingly soluble or is a stable complex. The solubility of the precipitate (or the dissociation of the complex) should be less than 5%. The addition of ethanol is sometimes recommended to reduce the solubility in the precipitations. An experimental curve is given in Fig. 6.8 (ammonium sulphate in aqueous-ethanol solution with barium acetate). If the solubility of the precipitate were negligibly small, the conductance at the equivalence point should be given by AB and not the observed AC. The addition of excess of the reagent depresses the solubility of the precipitate and, if the solubility is not too large, the position of the point B can be determined by continuing the straight portion of the two arms of the curve until they intersect.



#### 14. IONIC MOBILITY :

It is the speed of ion under unit potential gradient applied through solution.

$$u = \frac{\text{speed of ion (s)}}{\text{Potential gradient} \left( \frac{dV}{dx} \right)} = \frac{\text{cm}^2}{\text{volt} \cdot \text{sec.}} = \frac{\Lambda}{ZF}$$

$u/10^{-8} \text{ m}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$  in  $\text{H}_2\text{O}$  at 298 K

|                  |              |                  |      |               |       |                           |      |                    |      |                                 |      |               |       |
|------------------|--------------|------------------|------|---------------|-------|---------------------------|------|--------------------|------|---------------------------------|------|---------------|-------|
| $\text{Li}^+$    | 4.01<br>4.65 | $\text{Ca}^{+2}$ | 6.17 | $\text{Rb}^+$ | 7.92  | $\text{CH}_3\text{COO}^-$ | 7.92 | $\text{CO}_3^{--}$ | 7.91 | $\text{SO}_4^{--}$              | 8.29 | $\text{OH}^-$ | 20.64 |
| $\text{Na}^+$    | 5.19         | $\text{Ag}^+$    | 6.24 | $\text{H}^+$  | 7.92  | $\text{F}^-$              | 7.92 | $\text{Cl}^-$      | 7.96 | $[\text{Fe}(\text{CN})_6]^{3-}$ | 7.96 |               |       |
| $\text{Cu}^{+2}$ | 5.47<br>5.56 | $\text{NH}_4^+$  | 7.43 | $\text{H}^+$  | 36.23 | $\text{NO}_3^-$           | 7.40 | $\text{I}^-$       | 7.91 | $[\text{Fe}(\text{CN})_6]^{4-}$ | 11.4 |               |       |

**Ex.32** The resistance of a 1 N solution of salt is  $50 \Omega$ . Calculate the equivalent conductance of the solution, if the two platinum electrodes in solution are 2.1 cm apart and each having an area of  $4.2 \text{ cm}^2$ .

**Sol :**  $\kappa = \frac{1}{\rho} = \frac{1}{R} \left( \frac{\ell}{A} \right) = \frac{1}{50} \times \frac{2.1}{4.2} = \frac{1}{100}$  and  $\lambda_{\text{eq.}} = \frac{\kappa \times 1000}{N} = \frac{1}{100} \times \frac{1000}{1} = 10 = \Omega^{-1} \text{ cm}^2 \cdot \text{eq}^{-1}$

**Ex.33** Which of the following have maximum molar conductivity.

(i) 0.08 M solution and its specific conductivity is  $2 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$ .

(ii) 0.1 M solution and its resistivity is 50  $\Omega \text{cm}$ .

**Sol.** (i)  $\Lambda_m = \frac{\kappa \times 1000}{M} = 2 \times 10^{-2} \times \frac{1000}{0.08} = 250 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$

(ii)  $\Lambda_m = \frac{\kappa \times 1000}{M} \quad \therefore \kappa = \frac{1}{\rho} \quad \therefore \Lambda_m = \frac{1}{50} \times \frac{1000}{0.1} = 200 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$

So, the molar conductivity of 0.08 M solution will be greater than 0.1 M solution.

**Ex.34** The equivalent conductivity of  $\text{H}_2\text{SO}_4$  at infinite dilution is  $384 \Omega^{-1} \text{cm}^2 \text{eq}^{-1}$ . If 49 g  $\text{H}_2\text{SO}_4$  per litre is present in solution and specific resistance is 18.4  $\Omega\text{-cm}$  then calculate the degree of dissociation.

**Sol :** Equivalent of  $\text{H}_2\text{SO}_4 = \frac{49}{49} = 1 \text{ N}$

Specific conductance =  $\frac{1}{\text{specific resistance}} = \frac{1}{18.4}$

$\Rightarrow \lambda_{\text{eq.}} = \frac{1000 \times \kappa}{N} = \frac{1000 \times 1}{18.4} = 55$

Degree of dissociation ( $\alpha$ ) =  $\frac{\lambda_{\text{eq.}}^c}{\lambda_{\text{eq.}}^\infty} = \frac{55}{384}$   
 $= 0.14 \Rightarrow \alpha \% = 14\%$

**Ex.35** Explain following ionic conductance data of 25°C for various fatty acid anions.

| Anion       | Formula                                   | $\lambda^\circ$ AT 25°C (in $\text{ohm}^{-1}\text{cm}^2\text{eq}^{-1}$ ) |
|-------------|-------------------------------------------|--------------------------------------------------------------------------|
| Formate     | $\text{HCO}_2^-$                          | ~52                                                                      |
| Acetate     | $\text{CH}_3\text{CO}_2^-$                | 40.9                                                                     |
| Propionate  | $\text{CH}_3\text{CH}_2\text{CO}_2^-$     | 35.8                                                                     |
| Butyrate    | $\text{CH}_3(\text{CH}_2)_2\text{CO}_2^-$ | 32.6                                                                     |
| Valerianate | $\text{CH}_3(\text{CH}_2)_3\text{CO}_2^-$ | ~29                                                                      |
| Caproate    | $\text{CH}_3(\text{CH}_2)_4\text{CO}_2^-$ | ~28                                                                      |

**Sol.** With increasing chain length bulk increases decreasing ionic mobility and thus equivalent conductance decreases.

$\therefore$  Charge is identical  $\lambda_m$  also decreases.

**Ex.36** The resistance of a 0.01 N solution of an electrolyte was found to 210 ohm at 298 K using a conductivity cell with a cell constant of  $0.88 \text{cm}^{-1}$ . Calculate specific conductance and equivalent conductance of solution.

**Sol.** Given, for 0.01 N solution.

$R = 210 \text{ ohm} \quad , \quad \frac{l}{a} = 0.88 \text{cm}^{-1}$

Specific conductance,

$$\therefore \kappa = \frac{1}{R} \times \frac{\ell}{a} \Rightarrow \kappa = \frac{1}{210} \times 0.88 = 4.19 \times 10^{-3} \text{ mho cm}^{-1}$$

$$\Lambda_{\text{eq}} = \frac{\kappa \times 1000}{N} = \frac{4.19 \times 10^{-3} \times 1000}{0.01} = 419 \text{ mho cm}^2 \text{ eq}^{-1}.$$

**Ex.37** The conductivity of pure water in a conductivity cell with electrodes of cross-sectional area  $4 \text{ cm}^2$  placed at a distance  $2 \text{ cm}$  apart is  $8 \times 10^{-7} \text{ S cm}^{-1}$ . Calculate;

(a) The resistance of water.

(b) The current that would flow through the cell under the applied potential difference of  $1 \text{ volt}$ .

**Sol.** Cell constant  $= \frac{\ell}{a} = \frac{2}{4} = \frac{1}{2} \text{ cm}^{-1}$

(a) Also,  $\kappa = \frac{1}{R} \times \frac{\ell}{a}$

$$R = \frac{1}{\kappa} \times \frac{\ell}{a} = \frac{1}{8 \times 10^{-7}} \times \frac{1}{2} = 6.25 \times 10^5 \text{ ohm}$$

(b) From Ohm's law,  $\frac{V}{i} = R$

$$\therefore i = \frac{1}{6.25 \times 10^5} = 1.6 \times 10^{-6} \text{ ampere}$$

**Ex.38** Molar conductance of  $1 \text{ M}$  solution of weak acid  $\text{HA}$  is  $20 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . Find % dissociation of  $\text{HA}$  :

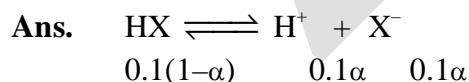
$$\left( \begin{array}{l} \Lambda_m^\circ(\text{H}^+) = 350 \text{ S cm}^2 \text{ mol}^{-1} \\ \Lambda_m^\circ(\text{A}^-) = 50 \text{ S cm}^2 \text{ mol}^{-1} \end{array} \right)$$

**Ans.**  $\Lambda_m^\circ(\text{HA}) = 350 + 50 = 400$

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^\circ} \times 100 = \frac{20}{400} \times 100 = 5 \%$$

**Ex.39** Conductivity of an aqueous solution of  $0.1 \text{ M HX}$  (a weak mono-protic acid) is  $5 \times 10^{-4} \text{ Sm}^{-1}$ .

Find  $pK_a[\text{HX}]$ . Given :  $\Lambda_m^\infty[\text{H}^+] = 0.04 \text{ Sm}^2 \text{ mol}^{-1}$  ;  $\Lambda_m^\infty[\text{X}^-] = 0.01 \text{ Sm}^2 \text{ mol}^{-1}$



$$\Lambda_m = k \times \frac{1000}{C} \Rightarrow 5 \times 10^{-4} \times \frac{1000}{0.1} = 0.05 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\infty} = \frac{0.05}{0.05} \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1} = 10^{-4}$$

$$K_a = C\alpha^2 = 0.1 \times (10^{-4})^2 = 10^{-9}$$

$$pK_a = 9$$

**Ex.40** Specific conductance of  $10^{-4}$  M n-Butyric acid aqueous solution is  $1.9 \times 10^{-9} \text{ S m}^{-1}$ . If molar conductance of n-Butyric acid at infinite dilution is  $380 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$ , then  $K_a$  for n-Butyric acid is :

**Sol.**  $\Lambda_m = 1000 \times \frac{1.9 \times 10^{-9}}{10^{-4}} = 1.9 \times 10^{-2}$

$$\alpha = \frac{1.9 \times 10^{-2}}{380 \times 10^{-4}} = 0.5$$

$$K_a = \frac{10^{-4}(0.5)^2}{1-0.5} = 5 \times 10^{-5} \text{ M}$$

**Ex.41** The specific conductance of a saturated AgCl solution is found to be  $2.12 \times 10^{-6} \text{ S cm}^{-1}$  and that for water is  $6 \times 10^{-8} \text{ S cm}^{-1}$ . The solubility of AgCl is :

$$(l_{eq.}^\circ = 103 \text{ S equiv}^{-1} \text{ cm}^2)$$

**Sol.**  $S_o = 241.67 \text{ S cm}^2 \text{ mol}^{-1}$

$$S = \frac{(F_{\text{Ag sol.}} - F_{\text{H}_2\text{O}}) \times 1000}{(\Lambda_{eq.}^0)_{\text{AgCl}}} = 2 \times 10^{-5} \text{ M}$$

**Ex.42** The value of  $\mu^\circ$  for  $\text{NH}_4\text{Cl}$ ,  $\text{NaOH}$  and  $\text{NaCl}$  are 129.8, 248.1 and  $126.4 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  respectively. Calculate  $\mu^\circ$  for  $\text{NH}_4\text{OH}$  solution.

**Sol.**  $\mu_{\text{NH}_4\text{OH}}^\circ = \mu_{\text{NH}_4\text{Cl}}^\circ + \mu_{\text{NaOH}}^\circ - \mu_{\text{NaCl}}^\circ$   
 $= 129.8 + 248.1 - 126.4$

$$\mu_{\text{NH}_4\text{OH}}^\circ = 251.5 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

**Ex.43** Calculate molar conductance for  $\text{NH}_4\text{OH}$ , given that molar conductances for  $\text{Ba(OH)}_2$ ,  $\text{BaCl}_2$  and  $\text{NH}_4\text{Cl}$  are 523.28, 280.0 and  $129.8 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  respectively.

**Sol.**  $\mu_{\text{Ba(OH)}_2}^\circ = \lambda_{\text{Ba}^{2+}}^\circ + 2\lambda_{\text{OH}^-}^\circ = 523.28$  ..... (i)

$$\mu_{\text{BaCl}_2}^\circ = \lambda_{\text{Ba}^{2+}}^\circ + 2\lambda_{\text{Cl}^-}^\circ = 280.00$$
 ..... (ii)

$$\mu_{\text{NH}_4\text{Cl}}^\circ = \lambda_{\text{NH}_4^+}^\circ + \lambda_{\text{Cl}^-}^\circ = 129.80$$
 ..... (iii)

$$\mu_{\text{NH}_4\text{OH}}^\circ = \lambda_{\text{NH}_4^+}^\circ + \lambda_{\text{OH}^-}^\circ = ?$$

$$\text{Eq. (iii)} + \frac{\text{Eq. (i)}}{2} - \frac{\text{Eq. (ii)}}{2} \text{ will gives}$$

$$\lambda_{\text{NH}_4^+}^\circ + \lambda_{\text{OH}^-}^\circ = \lambda_{\text{NH}_4\text{OH}}^\circ = \frac{502.88}{2} = 251.44 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

**Ex.44** The equivalent conductivities of acetic acid at 298 K at the concentrations of 0.1 M and 0.001 M are 5.20 and 49.2 S cm<sup>2</sup> eq.<sup>-1</sup> respectively. Calculate the degree of dissociation of acetic acid at these concentrations. Given that,  $\lambda^\infty(H^+)$  and  $\lambda^\infty(CH_3COO^-)$  are 349.8 and 40.9 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> respectively.

**Sol.** Degree of dissociation is given by  $\alpha = \frac{\lambda^c}{\lambda^\infty}$

(i) Evaluation of  $\lambda_{CH_3COOH}^\infty$  :

$$\begin{aligned}\lambda_{CH_3COOH}^\infty &= \lambda_{CH_3COO^-}^\infty + \lambda_{H^+}^\infty \\ &= 40.9 + 349.8 = 390.7 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq.}^{-1}\end{aligned}$$

(ii) Evaluation of degree of dissociation :

$$\text{At } C = 0.1 \text{ M } \alpha = \frac{\lambda^c}{\lambda^\infty} = \frac{5.20}{390.7} = 0.013$$

i.e. 1.3%

$$\text{At } C = 0.001 \text{ M } \alpha = \frac{\lambda^c}{\lambda^\infty} = \frac{49.2}{390.7} = 0.125$$

i.e. 12.5%

**Ex.45** At infinite dilution the molar conductance of  $Al^{+3}$  and  $SO_4^{-2}$  ion are 189 and 160  $\Omega^{-1} \text{ cm}^2 \text{ mole}^{-1}$  respectively. Calculate the equivalent and molar conductivity at infinite dilute of  $Al_2(SO_4)_3$ .

**Sol.**

$$\begin{aligned}\lambda_{eq[Al_2(SO_4)_3]}^\infty &= \frac{1}{3}\lambda_{Al^{+3}}^\infty + \frac{1}{2}\lambda_{SO_4^{2-}}^\infty \\ &= \frac{1}{3} \times 189 + \frac{1}{2} \times 160 \\ &= 143 \Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}\end{aligned}$$

$$\begin{aligned}\text{Molar conductivity} &= \lambda_{eq} \times \text{V. F.} = 143 \times 6 \\ &= 858 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}\end{aligned}$$

**Ex.46** Find  $\Lambda_m^\infty$  (in  $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ) for strong electrolyte  $\text{AB}_2$  in water at  $25^\circ$  from the following data.

|                                                         |      |     |
|---------------------------------------------------------|------|-----|
| Conc. C (mole/L)                                        | 0.25 | 1   |
| $\Lambda_m$ ( $\Omega^{-1} \text{ cm}^2 / \text{mol}$ ) | 160  | 150 |

**Sol.**  $160 = \Lambda_m^\infty - b \times \sqrt{.25} \quad \dots\text{(A)}$

$150 = \Lambda_m^\infty - b \times \sqrt{1} \quad \dots\text{(B)}$

$b = 20$  and  $\Lambda_m^\infty = 170$

$y = 170 - 20x$

Intercept = 170

$\Lambda_m^\infty = 170 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$

**Ex.47** For any sparingly soluble salt  $[\text{M}(\text{NH}_3)_4\text{Br}_2]\text{H}_2\text{PO}_2$

**Given :**  $\lambda_{\text{M}(\text{NH}_3)_4\text{Br}_2}^0 = 400 \text{ S-m}^2\text{-mol}^{-1}$ ,

$\lambda_{\text{H}_2\text{PO}_2}^0 = 100 \text{ S-m}^2\text{-mol}^{-1}$

Specific resistance of saturated  $[\text{M}(\text{NH}_3)_4\text{Br}_2]\text{H}_2\text{PO}_2$  solution is  $200 \Omega\text{-cm}$ .

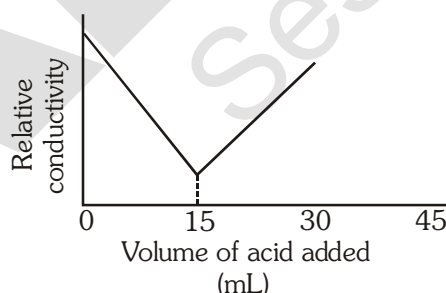
If solubility product constant of the above salt is  $10^{-x}$ . What will be the value of  $x$ .

**Ans.**  $\Lambda_m^\infty = \kappa \times \frac{1000}{m} \times 10^{-6}$

$500 = \frac{1}{200} \times \frac{1000}{5} \times 10^{-6}$

$S = 10^{-8} \text{ mol/L}$ ,  $K_{sp} = S^2 = 10^{-16}$

**Ex.48** 20 mL of KOH solution was titrated with 0.2 M  $\text{H}_2\text{SO}_4$  solution in a conductivity cell. The data obtained were plotted to give the graph shown below :



the concentration of KOH solution was -

(A) 0.3 M

(B) 0.15 M

(C) 0.12 M

(D) 0.075 M

**Sol.** (A)

$20 \times M = 0.2 \times 2 \times 15 \Rightarrow M = 0.15$



## ANSWER KEY

## EXERCISE # I

- |                    |                |                         |
|--------------------|----------------|-------------------------|
| 1. Ans. 1.61 V     | 2. Ans. 1.35 V | 3. Ans. - 0.80 V, $N_0$ |
| 4. Ans. - 0.0367 V | 5. Ans. (C)    | 6. Ans. (C)             |
| 7. Ans. (C)        | 8. Ans. (B)    | 9. Ans. (C)             |
| 10. Ans. (C)       | 11. Ans. (A)   |                         |
12. For a spontaneous reaction the  $\Delta G$ , equilibrium constant (K) and  $E_{\text{Cell}}^0$  will be respectively
- |              |              |              |
|--------------|--------------|--------------|
| 12. Ans. (C) | 13. Ans. (A) | 14. Ans. (D) |
| 15. Ans. (B) | 16. Ans. (A) | 17. Ans. (C) |
18. Ans.

## EXERCISE # II

19. Ans. (a)  $2\text{Ag} + \text{Cu}^{2+} \longrightarrow 2\text{Ag}^+ + \text{Cu}$ , (b)  $\text{MnO}_4^- + 5\text{Fe}^{2+} + 8\text{H}^+ \longrightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O}$   
 (c)  $2\text{Cl}^- + 2\text{Ag}^+ \longrightarrow 2\text{Ag} + \text{Cl}_2$ , (d)  $\text{H}_2 + \text{Cd}^{2+} \longrightarrow \text{Cd} + 2\text{H}^+$
20. Ans. (a)  $\text{Zn} | \text{Zn}^{2+} || \text{Cd}^{2+} | \text{Cd}$ , (b)  $\text{Pt}, \text{H}_2 | \text{H}^+ || \text{Ag}^+ | \text{Ag}$ ,  
 (c)  $\text{Pt} | \text{Fe}^{2+}, \text{Fe}^{3+} || \text{Cr}_2\text{O}_7^{2-}, \text{H}^+ | \text{Cr}^{3+} | \text{Pt}$
21. Ans.  $E = 1.159\text{V}$
22. Ans.  $E_{\text{cell}}^0 = +0.01\text{V}$ ,  $E_{\text{cell}} = -0.0785\text{V}$ , correct representation is  $\text{Pb} | \text{Pb}^{2+} (10^{-3}\text{M}) || \text{Sn}^{2+} (1\text{M}) | \text{Sn}$
23. Ans.  $[\text{Cu}^{2+}] = 2.97 \times 10^{-12}\text{M}$  for  $E = 0$
- |                                     |                                      |                            |
|-------------------------------------|--------------------------------------|----------------------------|
| 24. Ans. $K_c = 7.6 \times 10^{12}$ | 25. Ans. $K_c = 2.18 \times 10^{26}$ | 26. $E^0 = 0.7826\text{V}$ |
| 27. Ans. (7)                        | 28. Ans. 0.0295 V                    | 29. Ans. pH = 4            |
| 30. Ans. (B)                        | 31. Ans. (D)                         | 32. Ans. (C)               |
| 33. Ans. (A)                        | 34. Ans. (C)                         | 35. Ans. (B)               |
| 36. Ans. (D)                        | 37. Ans. (A)                         | 38. Ans. (C)               |
| 39. Ans. (B)                        | 40. Ans. (B)                         | 41. Ans. (C)               |
| 42. Ans. (A)                        | 43. Ans. (B)                         | 44. Ans. (A)               |
| 45. Ans. (A)                        | 46. Ans. (A)                         | 47. Ans. (D)               |
48. Ans. (D)

### EXERCISE # III

- |     |                                                                                                                                           |     |         |
|-----|-------------------------------------------------------------------------------------------------------------------------------------------|-----|---------|
| 49. | Ans. (a) $6.02 \times 10^{22}$ electrons lost, (b) $1.89 \times 10^{22}$ electrons gained, (c) (b) $1.80 \times 10^{23}$ electrons gained |     |         |
| 50. | Ans. (a) 0.75 F, (b) 0.69 F, (c) 1.1 F                                                                                                    |     |         |
| 51. | Ans. (i) 54 gm, (ii) 16.35 gm                                                                                                             |     |         |
| 52. | Ans. 0.112 litre                                                                                                                          |     |         |
| 53. | Ans. (i) 2.17 gm ; (ii) 1336. 15 sec                                                                                                      |     |         |
| 54. | Ans.(B)                                                                                                                                   | 55. | Ans.(C) |
| 57. | Ans.(A)                                                                                                                                   | 58. | Ans.(A) |
| 60. | Ans.(C)                                                                                                                                   | 61. | Ans.(A) |
| 63. | Ans.(D)                                                                                                                                   | 64. | Ans.(C) |
| 66. | Ans.(C)                                                                                                                                   | 67. | Ans.(A) |
| 69. | Ans.(B)                                                                                                                                   | 70. | Ans.(A) |
| 72. | Ans.(D)                                                                                                                                   | 73. | Ans.(C) |
|     |                                                                                                                                           | 56. | Ans.(A) |
|     |                                                                                                                                           | 59. | Ans.(C) |
|     |                                                                                                                                           | 62. | Ans.(A) |
|     |                                                                                                                                           | 65. | Ans.(B) |
|     |                                                                                                                                           | 68. | Ans.(A) |
|     |                                                                                                                                           | 71. | Ans.(C) |

## EXERCISE # IV

- |     |                                                                                                |             |             |
|-----|------------------------------------------------------------------------------------------------|-------------|-------------|
| 74. | Ans. $442 \text{ S cm}^2 \text{ equivalent}^{-1}$                                              |             |             |
| 75. | Ans. $0.00040 \text{ S cm}^{-1}$ ; $2500 \text{ ohm cm}$                                       |             |             |
| 76. | Ans. (i) $6.25 \times 10^5 \text{ ohm}$ , (ii) $1.6 \times 10^{-6} \text{ amp}$                |             |             |
| 77. | Ans. $0.0125 \text{ mho g equiv}^{-1} \text{ m}^2$ , $1.25 \times 10^{-3} \text{ mho cm}^{-1}$ |             |             |
| 78. | Ans. $0.8$                                                                                     |             |             |
| 79. | Ans. $10^{-10} \text{ mole}^2 \text{  litre}^2$                                                |             |             |
| 80. | Ans. (i) $400 \text{ S cm}^2 \text{ mol}^{-1}$ (ii) $12 \%$                                    |             |             |
| 81. | Ans. $510 \times 10^{-4} \text{ mho cm}^2 \text{ mol}^{-1}$                                    |             |             |
| 82. | Ans.(B)                                                                                        | 83. Ans.(D) | 84. Ans.(A) |
| 85. | Ans.(B)                                                                                        | 86. Ans.(B) | 87. Ans.(A) |
| 88. | Ans.(A)                                                                                        | 89. Ans.(A) | 90. Ans.(C) |
| 91. | Ans.(D)                                                                                        | 92. Ans.(C) | 93. Ans.(A) |
| 94. | Ans.(B))                                                                                       | 95. Ans.(C) | 96. Ans.(A) |

## SOME PREVIOUS YEAR SOLVED EXAMPLE

1. Find the solubility product of a saturated solution of  $\text{Ag}_2\text{CrO}_4$  in water at 298 K if the emf of the cell  $\text{Ag}|\text{Ag}^+ (\text{satd. Ag}_2\text{CrO}_4 \text{ soln.}) || \text{Ag}^+ (0.1 \text{ M}) | \text{Ag}$  is 0.164 V at 298K. [JEE 1998]

1. **Ans. ( $K_{\text{sp}} = 2.287 \times 10^{-12}$ )**

Sol.  $\text{Ag}|\text{Ag}^+ \text{ sat. soln.} || \text{Ag}^+ (0.1 \text{ M}) | \text{Ag}$   
 $\text{AgClO}_4$

$$0.164 = 0 - \frac{.059}{1} \log \frac{[\text{Ag}^+]_{\text{A}}}{0.1}$$

$$\therefore [\text{Ag}^+]_{\text{A}} = (1.66 \times 10^{-4}) \times (.83 \times 10^{-4})$$

$$= 2.287 \times 10^{-12}$$

2. Calculate the equilibrium constant for the reaction,  $2\text{Fe}^{3+} + 3\text{I}^- \rightleftharpoons 2\text{Fe}^{2+} + \text{I}_3^-$ . The standard reduction potentials in acidic conditions are 0.77 and 0.54 V respectively for  $\text{Fe}^{3+} | \text{Fe}^{2+}$  and  $\text{I}_3^- | \text{I}^-$  couples. [JEE 1998]

2. **Ans. ( $K_{\text{C}} = 6.26 \times 10^7$ )**

Sol.  $2\text{Fe}^{3+} + 3\text{I}^- \rightleftharpoons 2\text{Fe}^{2+} + \text{I}_3^-$

$$E^\circ = 0.77 + (-.54) = 0.23, \text{ Keq} = 10^{\frac{2 \times .23}{.059}}$$

$$\text{Keq} = 6.26 \times 10^7$$

3. A gas X at 1 atm is bubbled through a solution containing a mixture of 1 M Y and 1 M Z at 25°C. If the reduction potential of  $\text{Z} > \text{Y} > \text{X}$ , then [JEE 1999]

(A) Y will oxidise X and not Z

(B) Y will oxidise Z and X

(C) Y will oxidise both X and Z

(D) Y will reduce both X and Z.

3. **Ans. (A)**

4. The following electrochemical cell has been set up



$$E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.77 \text{ V and } E^\circ_{\text{Ce}^{4+}/\text{Ce}^{3+}} = 1.61 \text{ V}$$

If an ammeter is connected between the two platinum electrodes. predict the direction of flow of current. Will the current increase or decrease with time? [JEE 2000]

4. **Ans. (decrease with time)**

Sol.  $E^\circ_{\text{cell}}$  is (+) ve so cell will work and current will flow from cathode to anode. Current will decrease with time

5. Copper sulphate solution (250 mL) was electrolysed using a platinum anode and a copper cathode. A constant current of 2 mA was passed for 16 min. It was found that after electrolysis, the absorbance (concentration) of the solution was reduced to 50% of its original value. Calculate the concentration of copper sulphate in the solution to begin with. [JEE 2000]

5. **Ans. ( $7.95 \times 10^{-5} \text{ M}$ )**

$$\text{Sol. } (n_{\text{Cu}^{+2}})_{\text{reduced}} = \frac{2 \times 10^{-3} \times 16 \times 60}{96500 \times 2} = \frac{.96}{96500}$$

$$(n_{\text{Cu}^{+2}})_{\text{originally present}} = \frac{1.92}{96500}$$

$$\therefore M = \frac{1.92}{96500} \times \frac{1000}{250} = 7.958 \times 10^{-5}$$

$$E^\circ_{\text{cell}} = -.77 + 1.61 = 0.84$$

6. For the electrochemical cell,  $M | M^+ || X^- | X$ ,  $E^\circ (M^+|M) = 0.44 \text{ V}$  and  $E^\circ (X|X^-) = 0.33 \text{ V}$ . From this data, one can deduce that [JEE 2000]

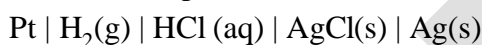
- (A)  $M + X \longrightarrow M^+ + X^-$  is the spontaneous reaction  
 (B)  $M^+ + X^- \longrightarrow M + X$  is the spontaneous reaction  
 (C)  $E_{\text{cell}} = 0.77 \text{ V}$   
 (D)  $E_{\text{cell}} = -0.77 \text{ V}$

6. **Ans.(B)**

$$\text{Sol. } E^\circ_{\text{cell}} = E^\circ_{\text{MM}^+} + E^\circ_{\text{M/M}^+} + E^\circ_{\text{X}^-/\text{X}} = -.44 + -.33 = -0.77 \text{ V}$$

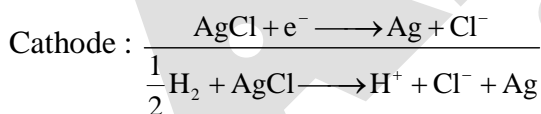
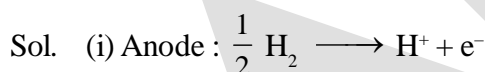
so (B)

7. The standard potential of the following cell is  $0.23 \text{ V}$  at  $15^\circ \text{C}$  &  $0.21 \text{ V}$  at  $35^\circ \text{C}$



- (i) Write the cell reaction.  
 (ii) Calculate  $\Delta H^\circ$ ,  $\Delta S^\circ$  for the cell reaction by assuming that these quantities remain unchanged in the range  $15^\circ \text{C}$  to  $35^\circ \text{C}$ .  
 (iii) Calculate the solubility of  $\text{AgCl}$  in water at  $25^\circ \text{C}$ . Given standard reduction potential of the  $\text{Ag}^+|\text{Ag}$  couple is  $0.80 \text{ V}$  at  $25^\circ \text{C}$ . [JEE 2001]

7. **Ans.  $\Delta H^\circ = -49987 \text{ J mol}^{-1}$ ,  $\Delta S^\circ = -96.5 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $s = 1.47 \times 10^{-5} \text{ M}$**



$$(ii) \frac{\partial E}{\partial T} = \frac{.21 - .23}{308 - 288} = \frac{.02}{10} = -2 \times 10^{-3}$$

$$\Delta G^\circ = -nFE^\circ \text{ so } (\Delta G^\circ)_{288\text{K}} = -22195 \text{ J } (\Delta G^\circ)_{308\text{K}} = -20265 \text{ J}$$

$$\text{now using } \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \Rightarrow \Delta H^\circ = -49987 \text{ J, } \Delta S^\circ = -96.5 \text{ J}$$

$$(iii) E^\circ_{25^\circ \text{C}} = 0.22 \text{ V } E^\circ_{\text{cell}} = E^\circ_{\text{Cl}^-/\text{AgCl}/\text{Ag}} = 0.22$$

$$\text{so } -.8 + 0.22 = \frac{0.59}{1} \log K_{\text{sp}}$$

$$\therefore K_{\text{sp}} = 1.47 \times 10^{-10} \Rightarrow S = 1.21 \times 10^{-5}$$

8. Saturated solution of  $\text{KNO}_3$  is used to make salt bridge because

- (A) velocity of  $\text{K}^+$  is greater than that of  $\text{NO}_3^-$   
 (B) velocity of  $\text{NO}_3^-$  is greater than that of  $\text{K}^+$   
 (C) velocities of both  $\text{K}^+$  and  $\text{NO}_3^-$  are nearly the same  
 (D)  $\text{KNO}_3$  is highly soluble in water

[JEE 2001]

8. **Ans.(C)**

Sol. Fact

9. The correct order of equivalent conductance at infinite dilution of  $\text{LiCl}$ ,  $\text{NaCl}$  and  $\text{KCl}$  is

- (A)  $\text{LiCl} > \text{NaCl} > \text{KCl}$  (B)  $\text{KCl} > \text{NaCl} > \text{LiCl}$   
 (C)  $\text{NaCl} > \text{KCl} > \text{LiCl}$  (D)  $\text{LiCl} > \text{KCl} > \text{NaCl}$

[JEE 2001]

9. **Ans.(B)**

Sol. Fact

10. The reaction,



is an example of

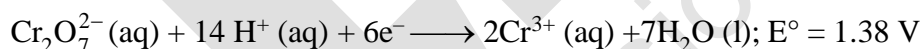
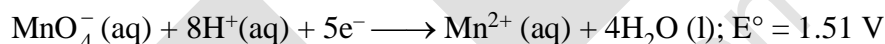
- (A) Oxidation reaction (B) Reduction reaction  
 (C) Disproportionation reaction (D) Decomposition reaction

[JEE 2001]

10. **Ans.(C)**

Sol. Fact

11. Standard electrode potential data are useful for understanding the suitability of an oxidant in a redox titration. Some half cell reactions and their standard potentials are given below: [JEE 2002]



Identify the only incorrect statement regarding quantitative estimation of aqueous  $\text{Fe}(\text{NO}_3)_2$

- (A)  $\text{MnO}_4^-$  can be used in aqueous  $\text{HCl}$   
 (B)  $\text{Cr}_2\text{O}_7^{2-}$  can be used in aqueous  $\text{HCl}$   
 (C)  $\text{MnO}_4^-$  can be used in aqueous  $\text{H}_2\text{SO}_4$   
 (D)  $\text{Cr}_2\text{O}_7^{2-}$  can be used in aqueous  $\text{H}_2\text{SO}_4$

11. **Ans.(A)**

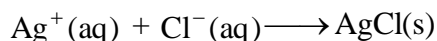
Sol.  $\text{MnO}_4^-$  will oxidise  $\text{Cl}^-$  into  $\text{Cl}_2$  so  $\text{MnO}_4^-$  can not be used in aqueous  $\text{HCl}$



Sol.  $0.2905 = E^\circ - \frac{.059}{2} \log \frac{.1}{0.01} \Rightarrow E^\circ = .32$

$\therefore K_{sp} = 10^{\frac{2 \times .32}{.0591}} = 10^{\frac{.32}{.0295}} \Rightarrow B$

16. (a) Calculate  $\Delta G_f^\circ$  of the following reaction



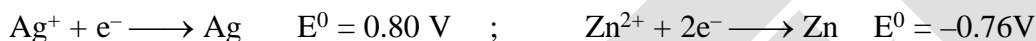
Given :  $\Delta G_f^\circ(\text{AgCl}) = -109 \text{ kJ/mole}$ ,  $\Delta G_f^\circ(\text{Cl}^-) = -129 \text{ kJ/mole}$ ,  $\Delta G_f^\circ(\text{Ag}^+) = 77 \text{ kJ/mole}$

Represent the above reaction in form of a cell

Calculate  $E^\circ$  of the cell. Find  $\log_{10} K_{sp}$  of AgCl

(b)  $6.539 \times 10^{-2} \text{ g}$  of metallic Zn (amu = 65.39) was added to 100 ml of saturated solution of AgCl.

Calculate  $\log_{10} \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2}$ , given that



Also find how many moles of Ag will be formed?

[JEE 2005]

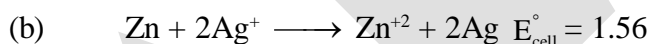
16. **Ans.(a)  $E^\circ = 0.59 \text{ V}$ ,  $\log_{10} K_{sp} = -10$  (b) 52.8,  $10^{-6}$  moles**

Sol. (a)  $\Delta G^\circ = (-109) - [-129 + 77] = -57$

$$E^\circ = \frac{-57 \times 1000}{1 \times 96500} = 0.59$$

$$\Delta G^\circ = -2.303RT \log K_{sp} \Rightarrow \log K_{sp} = \frac{-57 \times 1000}{-2.303 \times 8.314 \times 298}$$

$$\log K_{sp} = 9.989 \cong 10$$



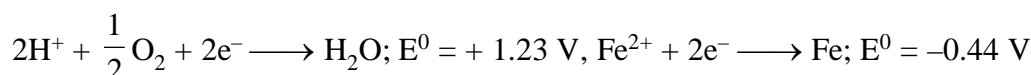
$$\therefore \log_{10} \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2} = \frac{1.56 \times 2}{.059} = 52.8$$

$$[\text{Ag}^+] = \sqrt{K_{sp}} = \sqrt{10^{-10}} = 10^{-5}$$

$$\therefore n_{\text{Ag}^+} = 10^{-5} \times .1 = 10^{-6}$$

17. The half cell reactions for rusting of iron are:

[JEE 2005]



$\Delta G^\circ$  (in kJ) for the reaction is:

(A) -76

(B) -322

(C) -122

(D) -176

17. **Ans.(B)**

Sol.  $\Delta G^\circ = -nFE^\circ$

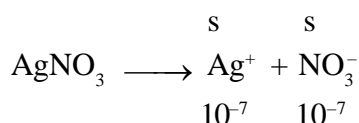
$$= \frac{-2 \times 96500 \times 1.67}{1000} - 322$$

18. We have taken a saturated solution of AgBr.  $K_{sp}$  of AgBr is  $12 \times 10^{-14}$ . If  $10^{-7}$  mole of  $\text{AgNO}_3$  are added to 1 litre of this solution find conductivity (specific conductance) of this solution in terms of  $10^{-7} \text{ S m}^{-1}$  [JEE 2006]

Given :  $\lambda_{(\text{Ag}^+)}^0 = 6 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}$  ;  $\lambda_{(\text{Br}^-)}^0 = 8 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}$  ;  $\lambda_{(\text{NO}_3^-)}^0 = 7 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}$

18. Ans. (55  $\text{S m}^{-1}$ )

Sol.  $\text{AgBr} \rightleftharpoons \text{Ag}^+ + \text{Br}^-$



$$\therefore (K_{sp})_{\text{AgBr}} = [\text{Ag}^+][\text{Br}^-] \Rightarrow 12 \times 10^{-14} = (s + 10^{-7}) \cdot (s)$$

$$s^2 + 10^{-7}s - 12 \times 10^{-14} = 0 \Rightarrow s = 3 \times 10^{-7}$$

$$\therefore [\text{Ag}^+] = 4 \times 10^{-7} [\text{Br}^-] = 3 \times 10^{-7} [\text{NO}_3^-] = 10^{-7}$$

$$\text{now } \Lambda_M^\infty = \frac{1000k}{M}$$

$$\text{for } \text{Ag}^+ \Rightarrow 6 \times 10^{-3} \times 10^4 = \frac{1000k}{4 \times 10^{-7}} \Rightarrow k_{\text{Ag}^+} = 24$$

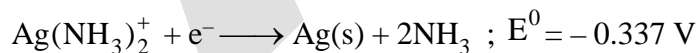
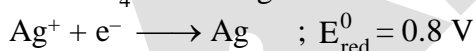
$$\text{Br}^- \Rightarrow 8 \times 10^{-3} \times 10^4 = \frac{1000k}{3 \times 10^{-7}} \Rightarrow k_{\text{Br}^-} = 24$$

$$\text{NO}_3^- \Rightarrow 7 \times 10^{-3} \times 10^4 = \frac{1000k}{10^{-7}} \Rightarrow R_{\text{NO}_3^-} = 7$$

Ans. 55

### Question No. 19 to 21 (3 questions)

Tollen's reagent is used for the detection of aldehyde when a solution of  $\text{AgNO}_3$  is added to glucose with  $\text{NH}_4\text{OH}$  then gluconic acid is formed



$$\left[ \text{Use } 2.303 \times \frac{RT}{F} = 0.0592 \text{ and } \frac{F}{RT} = 38.92 \text{ at } 298 \text{ K} \right]$$

[JEE 2006]

19.  $2\text{Ag}^+ + \text{C}_6\text{H}_{12}\text{O}_6 + \text{H}_2\text{O} \longrightarrow 2\text{Ag(s)} + \text{C}_6\text{H}_{12}\text{O}_7 + 2\text{H}^+$

Find  $\ln K$  of this reaction

(A) 66.13

(B) 58.38

(C) 28.30

(D) 46.29

19. Ans. (A)

$$\text{Sol. } \log K = \frac{2.303 \times n \times E^\circ}{.059} = \frac{2.303 \times 2 \times .85}{.059} = 66.13$$



20. When ammonia is added to the solution, pH is raised to 11. Which half-cell reaction is affected by pH and by how much?

- (A)  $E_{\text{oxd}}$  will increase by a factor of 0.65 from  $E_{\text{oxd}}^0$   
 (B)  $E_{\text{oxd}}$  will decrease by a factor of 0.65 from  $E_{\text{oxd}}^0$   
 (C)  $E_{\text{red}}$  will increase by a factor of 0.65 from  $E_{\text{red}}^0$   
 (D)  $E_{\text{red}}$  will decrease by a factor of 0.65 from  $E_{\text{red}}^0$

20. **Ans.(A)**

Sol. Since  $\text{H}^+$  is involved in oxidation half reaction so  $E_{\text{oxd}}$  will be affected and it will increase

$$E_{\text{oxd}} = E_{\text{oxd}}^0 - \frac{.059}{2} \log \frac{[\text{C}_6\text{H}_{12}\text{O}_7][\text{H}^+]^2}{[\text{C}_2\text{H}_{12}\text{O}_6]}$$

21. Ammonia is always added in this reaction. Which of the following must be incorrect?

- (A)  $\text{NH}_3$  combines with  $\text{Ag}^+$  to form a complex.  
 (B)  $\text{Ag}(\text{NH}_3)_2^+$  is a weaker oxidising reagent than  $\text{Ag}^+$ .  
 (C) In absence of  $\text{NH}_3$  silver salt of gluconic acid is formed.  
 (D)  $\text{NH}_3$  has affected the standard reduction potential of glucose|gluconic acid electrode.

21. **Ans.(D)**

Sol.  $E_{\text{Red}}^0$  in a constant quantity

**Paragraph for Question Nos. 22 to 24 (3 questions)**

Chemical reactions involve interaction of atoms and molecules. A large number of atoms|molecules (approximately  $6.023 \times 10^{23}$ ) are present in a few grams of any chemical compound varying with their atomic|molecular masses. To handle such large numbers conveniently, the mole concept was introduced. This concept has implications in diverse areas such as analytical chemistry, biochemistry, electrochemistry and radiochemistry. The following example illustrates a typical case, involving chemical|electrochemical reaction, which requires a clear understanding of the mole concept.

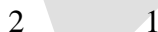
A 4.0 molar aqueous solution of NaCl is prepared and 500 mL of this solution is electrolysed. This leads to the evolution of chlorine gas at one of the electrodes (**atomic mass : Na = 23, Hg = 200; 1 Faraday = 96500 coulombs**) **[JEE 2007]**

22. The total number of moles of chlorine gas evolved is

- (A) 0.5 (B) 1.0 (C) 2.0 (D) 3.0

22. **Ans.(B)**

Sol. At anode  $2\text{Cl}^- \longrightarrow \text{Cl}_2 + 2\text{e}^-$

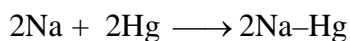


23. If the cathode is a Hg electrode, the maximum weight (g) of amalgam formed from this solution is

- (A) 200 (B) 225 (C) 400 (D) 446

23. **Ans.(D)**

Sol. At cathode  $2\text{Na}^+ + 2\text{e}^- \longrightarrow 2\text{Na(s)}$



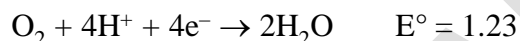
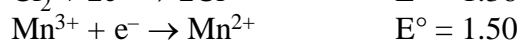
24. The total charge (coulombs) required for complete electrolysis is  
(A) 24125 (B) 48250 (C) 96500 (D) 193000

24. **Ans.(D)**

Sol. 2 moles on  $e^- = 2F = 193000 \text{ C}$

**Paragraph for Question Nos. 25 & 26 (2 questions)**

Redox reactions play a pivoted role in chemistry and biology. The values of standard redox potential ( $E^\circ$ ) of two half-cell reactions decide which way the reaction is expected to proceed. A simple example is a Daniel cell in which zinc goes into solution and copper gets deposited. Given below are a set of half-cell reactions (acidic medium) along with their  $E^\circ$  (V with respect to normal hydrogen electrode) values. Using this data obtain the correct explanations to Questions 14-16.



[JEE 2007]

25. Among the following, identify the correct statement.

(A) Chloride ion is oxidised by  $\text{O}_2$

(B)  $\text{Fe}^{2+}$  is oxidised by iodine

(C) Iodine ion is oxidised by chlorine

(D)  $\text{Mn}^{2+}$  is oxidised by chlorine

25. **Ans.(C)**

Sol. as  $E^\circ$  will be positive

26. While  $\text{Fe}^{3+}$  is stable,  $\text{Mn}^{3+}$  is not stable in acid solution because

(A)  $\text{O}_2$  oxidises  $\text{Mn}^{2+}$  to  $\text{Mn}^{3+}$

(B)  $\text{O}_2$  oxidises both  $\text{Mn}^{2+}$  to  $\text{Mn}^{3+}$  and  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$

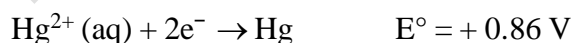
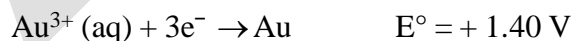
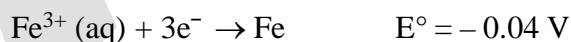
(C)  $\text{Fe}^{3+}$  oxidises  $\text{H}_2\text{O}$  to  $\text{O}_2$

(D)  $\text{Mn}^{3+}$  oxidises  $\text{H}_2\text{O}$  to  $\text{O}_2$

26. **Ans.(D)**

Sol. as  $E^\circ$  will be positive

28. For the reaction of  $\text{NO}_3^-$  ion in an aqueous solution,  $E^\circ$  is +0.96 V. Values of  $E^\circ$  for some metal ions are given below



The pair(s) of metal that is(are) oxidised by  $\text{NO}_3^-$  in aqueous solution is(are) [JEE 2009]

(A) V and Hg

(B) Hg and Fe

(C) Fe and Au

(D) Fe and V

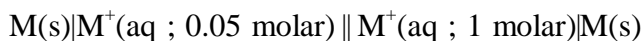
28. **Ans.(A,B,D)**

Sol. (A,B,D) as  $E^\circ$  will be positive

## Paragraph for Questions 29 to 30

The concentration of potassium ions inside a biological cell is at least twenty times higher than the outside. The resulting potential difference across the cell is important in several processes such as transmission of nerve impulses and maintaining the ion balance. A simple model for such a concentration cell involving a metal M is :

[JEE 2010]



For the above electrolytic cell the magnitude of the cell potential  $|E_{\text{cell}}| = 70 \text{ mV}$ .

29. For the above cell :-

(A)  $E_{\text{cell}} < 0$  ;  $\Delta G > 0$

(B)  $E_{\text{cell}} > 0$  ;  $\Delta G < 0$

(C)  $E_{\text{cell}} < 0$  ;  $\Delta G^0 > 0$

(D)  $E_{\text{cell}} > 0$  ;  $\Delta G^0 < 0$

29. **Ans.(B)**

Sol.  $E_1 = -\frac{.059}{1} \log \frac{.05}{1} = (+)\text{ve} \Rightarrow \text{so}$

30. If the 0.05 molar solution of  $M^+$  is replaced by a 0.0025 molar  $M^+$  solution, then the magnitude of the cell potential would be :-

(A) 35 mV

(B) 70 mV

(C) 140 mV

(D) 700 mV

30. **Ans.(C)**

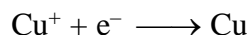
Sol.  $E_2 = -\frac{.059}{1} \log \frac{0.0025}{1}$   
 $= 2 \times E_1 = 140 \text{ mV} \Rightarrow \text{so}$

EXERCISE (S-I)

ELECTRODE POTENTIAL CELL EMF.

1. If for the half cell reactions  $\text{Cu}^{2+} + e^- \longrightarrow \text{Cu}^+$   $E^\circ = 0.15 \text{ V}$   
 $\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}$   $E^\circ = 0.34 \text{ V}$

Calculate  $E^\circ$  of the half cell reaction

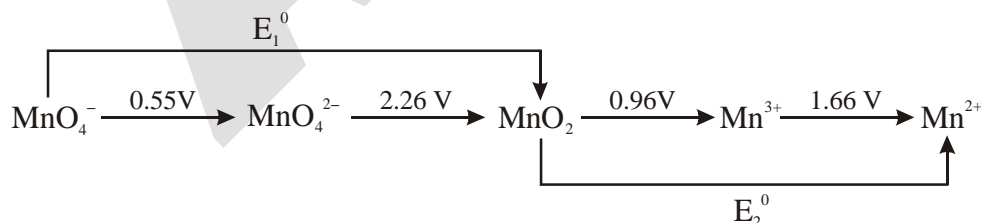


also predict whether  $\text{Cu}^+$  undergoes disproportionation or not.

2. For a cell  $\text{Mg(s)} | \text{Mg}^{2+}(\text{aq}) || \text{Ag}^+(\text{aq}) | \text{Ag}$ ,  
 (i) Calculate the equilibrium constant at  $25^\circ\text{C}$ .  
 (ii) Also find the maximum work per mole Mg that can be obtained by operating the cell in standard condition.  
 $E^\circ_{(\text{Mg}^{2+}|\text{Mg})} = -2.37\text{V}$ ,  $E^\circ_{(\text{Ag}^+|\text{Ag})} = 0.8 \text{ V}$ .
3. The  $\text{pK}_{\text{sp}}$  of AgI is 16.07. If the  $E^\circ$  value for  $\text{Ag}^+ | \text{Ag}$  is 0.7991 V. Find the  $E^\circ$  for the half cell reaction  $\text{AgI(s)} + e^- \longrightarrow \text{Ag} + \text{I}^-$ .
4. A zinc electrode is placed in a 0.1M solution at  $25^\circ\text{C}$ . Assuming that the salt ( $\text{ZnX}$ ) is 20% dissociated at this dilutions calculate the electrode reduction potential.  $E^\circ(\text{Zn}^{2+} | \text{Zn}) = -0.76\text{V}$ .

EQUILIBRIUM CONSTANT :

5. The standard reduction potential at  $25^\circ\text{C}$  for the reduction of water  
 $2\text{H}_2\text{O} + 2e^- \rightleftharpoons \text{H}_2 + 2\text{OH}^-$  is  $-0.8277 \text{ volt}$ . Calculate the equilibrium constant for the reaction  
 $2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$  at  $25^\circ\text{C}$ .
6. For the reaction,  $4\text{Al(s)} + 3\text{O}_2(\text{g}) + 6\text{H}_2\text{O} + 4 \text{OH}^- \rightleftharpoons 4 [\text{Al}(\text{OH})_4^-]$ ;  $E^\circ_{\text{cell}} = 2.73 \text{ V}$ .  
 If  $\Delta G_f^\circ(\text{OH}^-) = -157 \text{ kJ mol}^{-1}$  and  $\Delta G_f^\circ(\text{H}_2\text{O}) = -237.2 \text{ kJ mol}^{-1}$ , determine  $\Delta G_f^\circ[\text{Al}(\text{OH})_4^-]$ .
7. For the cell reaction :  
 $\text{Hg}_2\text{Cl}_2(\text{s}) + 2\text{Ag(s)} \rightarrow 2\text{Hg(l)} + 2\text{AgCl(s)}$   
 temperature coefficient of cell emf is found to be  $0.02 \text{ VK}^{-1}$ . Find  $\Delta_r S^\circ$  for cell reaction in  $\text{kJ mole}^{-1}$
8. From the standard potential in acidic medium as shown in the following latimer diagram, the value of  $(E_1^\circ + E_2^\circ)$ , in volts, is -



CONCENTRATION CELLS :

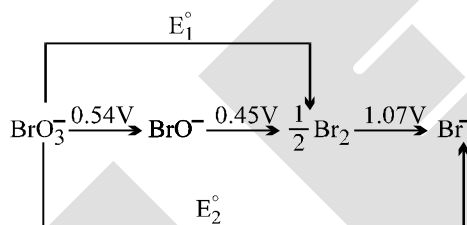
9. Equinormal Solutions of two weak acids, HA ( $\text{pK}_a = 3$ ) and HB ( $\text{pK}_a = 5$ ) are each placed in contact with equal pressure of hydrogen electrode at  $25^\circ\text{C}$ . When a cell is constructed by interconnecting them through a salt bridge, find the emf of the cell.



## EXERCISE (S-II)

- Calculate the emf of the cell  
 $\text{Pt}, \text{H}_2(1.0 \text{ atm}) | \text{CH}_3\text{COOH} (0.1\text{M}) || \text{NH}_3(\text{aq}, 0.01\text{M}) | \text{H}_2 (1.0 \text{ atm}),$   
 $\text{Pt } K_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}, K_b(\text{NH}_3) = 1.8 \times 10^{-5}.$
- The Edison storage cell is represented as  $\text{Fe}(\text{s}) | \text{FeO}(\text{s}) | \text{KOH}(\text{aq}) | \text{Ni}_2\text{O}_3(\text{s}) | \text{NiO}(\text{s})$  The half-cell reaction are  
 $\text{Ni}_2\text{O}_3(\text{s}) + \text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightleftharpoons 2\text{NiO}(\text{s}) + 2\text{OH}^-, \quad E^0 = +0.40\text{V}$   
 $\text{FeO}(\text{s}) + \text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightleftharpoons \text{Fe}(\text{s}) + 2\text{OH}^-, \quad E^0 = -0.87\text{V}$ 
  - What is the cell reaction?
  - What is the cell e.m.f.? How does it depend on the concentration of KOH?
  - What is the maximum amount of electrical energy that can be obtained from one mole of  $\text{Ni}_2\text{O}_3$ ?
- The standard reduction potential for  $\text{Cu}^{2+} | \text{Cu}$  is 0.34 V. Calculate the reduction potential at  $\text{pH} = 14$  for the above couple.  $K_{\text{sp}}$  of  $\text{Cu}(\text{OH})_2$  is  $1 \times 10^{-19}$ .
- The emf of the cell  $\text{Ag} | \text{AgI} | \text{KI}(0.05\text{M}) || \text{AgNO}_3(0.05\text{M}) | \text{Ag}$  is 0.788V. Calculate the solubility product of AgI.
- Consider the cell  $\text{Ag} | \text{AgBr}(\text{s}) | \text{Br}^- || \text{Cl}^- | \text{AgCl}(\text{s}) | \text{Ag}$  at  $25^\circ\text{C}$ . The solubility product constants of AgBr & AgCl are respectively  $5 \times 10^{-13}$  &  $1 \times 10^{-10}$ . For what ratio of the concentrations of  $\text{Br}^-$  &  $\text{Cl}^-$  ions would the emf of the cell be zero?
- For the galvanic cell :  $\text{Ag} | \text{AgCl}(\text{s}) | \text{KCl} (0.2\text{M}) || \text{KBr} (0.001 \text{ M}) | \text{AgBr}(\text{s}) | \text{Ag}$ ,  
 Calculate the EMF generated and assign correct polarity to each electrode for a spontaneous process after taking into account the cell reaction at  $25^\circ\text{C}$ .  
 $[K_{\text{sp}}(\text{AgCl}) = 2.8 \times 10^{-10}; K_{\text{sp}}(\text{AgBr}) = 3.3 \times 10^{-13}]$
- Given,  $E^0 = -0.268 \text{ V}$  for the  $\text{Cl}^- | \text{PbCl}_2 | \text{Pb}$  couple and  $-0.126 \text{ V}$  for the  $\text{Pb}^{2+} | \text{Pb}$  couple, determine  $K_{\text{sp}}$  for  $\text{PbCl}_2$  at  $25^\circ\text{C}$ ?
- Calculate the equilibrium constant for the reaction:  
 $3\text{Sn}(\text{s}) + 2\text{Cr}_2\text{O}_7^{2-} + 28\text{H}^+ \longrightarrow 3\text{Sn}^{4+} + 4\text{Cr}^{3+} + 14\text{H}_2\text{O}$   
 $E^0$  for  $\text{Sn} | \text{Sn}^{2+} = 0.136 \text{ V}$      $E^0$  for  $\text{Sn}^{2+} | \text{Sn}^{4+} = -0.154 \text{ V}$   
 $E^0$  for  $\text{Cr}_2\text{O}_7^{2-} | \text{Cr}^{3+} = 1.33 \text{ V}$
- One of the methods of preparation of per disulphuric acid,  $\text{H}_2\text{S}_2\text{O}_8$ , involve electrolytic oxidation of  $\text{H}_2\text{SO}_4$  at anode ( $2\text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{S}_2\text{O}_8 + 2\text{H}^+ + 2\text{e}^-$ ) with oxygen and hydrogen as by-products. In such an electrolysis, 9.722 L of  $\text{H}_2$  and 2.35 L of  $\text{O}_2$  were generated at STP. What is the weight of  $\text{H}_2\text{S}_2\text{O}_8$  formed?
- A current of 3 amp was passed for 2 hour through a solution of  $\text{CuSO}_4$ , 3 g of  $\text{Cu}^{2+}$  ions were deposited as Cu at cathode. Calculate percentage current efficiency of the process.
- Dal lake has water  $8.2 \times 10^{12}$  litre approximately. A power reactor produces electricity at the rate of  $1.5 \times 10^6$  coulomb per second at an appropriate voltage. How many years would it take to electrolyse the lake?

12. The equivalent conductance of 0.10 N solution of  $\text{MgCl}_2$  is  $97.1 \text{ mho cm}^2 \text{ eq}^{-1}$  at  $25^\circ\text{C}$ . a cell with electrode that are  $1.5 \text{ cm}^2$  in surface area and  $0.5 \text{ cm}$  apart is filled with  $0.1 \text{ N MgCl}_2$  solution. How much current will flow when potential difference between the electrodes is  $5 \text{ volt}$ .
13. When a solution of specific conductance  $1.342 \text{ ohm}^{-1} \text{ metre}^{-1}$  was placed in a conductivity cell with parallel electrodes, the resistance was found to be  $170.5 \text{ ohm}$ . Area of electrodes is  $1.86 \times 10^{-4} \text{ m}^2$ . Calculate separation of electrodes.
14. The specific conductance at  $25^\circ\text{C}$  of a saturated solution of  $\text{SrSO}_4$  is  $1.482 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$  while that of water used is  $1.5 \times 10^{-6} \text{ mho cm}^{-1}$ . Determine at  $25^\circ\text{C}$  the solubility in gm per litre of  $\text{SrSO}_4$  in water. Molar ionic conductance of  $\text{Sr}^{2+}$  and  $\text{SO}_4^{2-}$  ions at infinite dilution are  $59.46$  and  $79.8 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$  respectively. [  $\text{Sr} = 87.6$ ,  $\text{S} = 32$ ,  $\text{O} = 16$  ]
15. The EMF of the cell  $\text{M} | \text{M}^{n+} (0.02\text{M}) || \text{H}^+ (1\text{M}) | \text{H}_2(\text{g}) (1 \text{ atm}), \text{Pt}$  at  $25^\circ\text{C}$  is  $0.81\text{V}$ . Calculate the valency of the metal if the standard oxidation of the metal is  $0.76\text{V}$ .
16. From the standard potentials shown in the following diagram, calculate the potentials  $E_1^\circ$  and  $E_2^\circ$ .



17. Calculate the EMF of the cell,  
 $\text{Zn} - \text{Hg}(c_1\text{M}) | \text{Zn}^{2+}(\text{aq}) | \text{Hg} - \text{Zn}(c_2\text{M})$   
 at  $25^\circ\text{C}$ , if the concentrations of the zinc amalgam are:  $c_1 = 10\text{g}$  per  $100\text{g}$  of mercury and  $c_2 = 1\text{g}$  per  $100\text{g}$  of mercury.
18. How long a current of  $2\text{A}$  has to be passed through a solution of  $\text{AgNO}_3$  to coat a metal surface of  $80\text{cm}^2$  with  $5\mu\text{m}$  thick layer? Density of silver =  $10.8\text{g/cm}^3$ .
19.  $10\text{g}$  solution of  $\text{CuSO}_4$  is electrolyzed using  $0.01\text{F}$  of electricity. Calculate:  
 (a) The weight of resulting solution  
 (b) Equivalents of acid or alkali in the solution.
20. Cadmium amalgam is prepared by electrolysis of a solution of  $\text{CdCl}_2$  using a mercury cathode. How long should a current of  $5\text{A}$  be passed in order to prepare  $12\%$   $\text{Cd-Hg}$  amalgam on a cathode of  $2\text{gm Hg}$  ( $\text{Cd} = 112.4$ )

# EXERCISE (O-I)

## GALVANIC CELL

- The thermodynamic efficiency of cell is given by-  
 (A)  $\frac{\Delta H}{\Delta G}$  (B)  $\frac{nFE_{\text{cell}}}{\Delta G}$  (C)  $-\frac{nFE_{\text{cell}}}{\Delta H}$  (D) Zero
- From the following  $E^\circ$  values of half cells,  
 (i)  $A + e \rightarrow A^-$ ;  $E^\circ = -0.24 \text{ V}$  (ii)  $B^- + e \rightarrow B^{2-}$ ;  $E^\circ = +1.25 \text{ V}$   
 (iii)  $C^- + 2e \rightarrow C^{3-}$ ;  $E^\circ = -1.25 \text{ V}$  (iv)  $D + 2e \rightarrow D^{2-}$ ;  $E^\circ = +0.68 \text{ V}$   
 What combination of two half cells would result in a cell with the largest potential ?  
 (A) (ii) and (iii) (B) (ii) and (iv) (C) (i) and (iii) (D) (i) and (iv)
- Which of the following will increase the voltage of the cell with following cell reaction  
 $\text{Sn}_{(s)} + 2\text{Ag}^+_{(aq)} \rightarrow \text{Sn}^{2+}_{(aq)} + 2\text{Ag}_{(s)}$   
 (A) Decrease in the concentration of  $\text{Ag}^+$  ions  
 (B) Increase in the concentration of  $\text{Sn}^{2+}$  ions  
 (C) Increase in the concentration of  $\text{Ag}^+$  ions  
 (D) (A) & (B) both
- The standard emf for the cell reaction,  
 $\text{Zn}_{(s)} + \text{Cu}^{2+}_{(aq)} \rightarrow \text{Zn}^{2+}_{(aq)} + \text{Cu}_{(s)}$  is 1.10 volt at  $25^\circ\text{C}$ . The emf for the cell reaction when 0.1 M  $\text{Cu}^{2+}$  and 0.1 M  $\text{Zn}^{2+}$  solution are used at  $25^\circ\text{C}$  is :  
 (A) 1.10 volt (B) 0.110 volt (C) -1.10 volt (D) -0.110 volt
- What is the potential of the cell containing two hydrogen electrodes as represented below  
 $\text{Pt} | \text{H}_2(\text{g}) | \text{H}^+_{(\text{aq})}(10^{-8} \text{ M}) || \text{H}^+_{(\text{aq})}(0.001 \text{ M}) | \text{H}_2(\text{g}) | \text{Pt}$   
 (A) - 0.295 V (B) - 0.0591 V (C) 0.295 V (D) 0.0591 V
- Consider the cell,  $\text{Cu}|\text{Cu}^{2+}||\text{Ag}^+|\text{Ag}$ . If the concentration of  $\text{Cu}^{2+}$  and  $\text{Ag}^+$  ions becomes ten times the emf of the cell :-  
 (A) Becomes 10 times (B) Remains same  
 (C) Increase by 0.0295 V (D) Decrease by 0.0295 V
- The standard emf of a galvanic cell involving cell reaction with  $n = 4$  is found to be 0.295 V at  $25^\circ\text{C}$ . The equilibrium constant of the reaction would be,  
 (A)  $1.0 \times 10^{20}$  (B)  $2.0 \times 10^{11}$  (C)  $4.0 \times 10^{12}$  (D)  $1.0 \times 10^2$
- By how much times will potential of half cell  $\text{Cu}^{2+}|\text{Cu}$  change if, the solution is diluted to 100 times at 298 K :-  
 (A) Increases by 59 mV (B) Decrease by 59 mV  
 (C) Increases by 29.5 mV (D) Decreases by 29.5 mV



## ELECTROLYTIC CELL

9. When an electric current is passed through a cell containing an electrolyte, positive ions move towards the cathode and negative ions towards the anode. What will happen if the cathode is pulled out of the solution?
- (A) The positive ions will start moving towards the anode and negative ions will stop moving.  
 (B) The negative ions will continue to move towards the anode and the positive ions will stop moving  
 (C) Both positive and negative ions will move towards the anode.  
 (D) None of these movements will take place.
10. Electrolysis of a  $\text{CuSO}_4$  produces :—
- (A) An increase in pH (B) A decrease in pH  
 (C) Either decrease or increase (D) None
11. The same amount of electricity was passed through two separate electrolytic cells containing solutions of nickel nitrate  $[\text{Ni}(\text{NO}_3)_2]$  and chromium nitrate  $[\text{Cr}(\text{NO}_3)_3]$  respectively. If 0.3 g of nickel was deposited in the first cell, the amount of chromium deposited is :  
 (at. wt. of Ni = 59, at. wt. of Cr = 52)
- (A) 0.1 g (B) 0.17 g (C) 0.3 g (D) 0.6 g
12. The electric charge for electro deposition of 1 equivalent of a substance is :
- (A) one ampere per second (B) 4 faraday  
 (C) one ampere for one hour (D) charge on one mole of electrons
13. 3.17 g., of a substance was deposited by the flow of 0.1 mole of electrons. The equivalent weight of the substance is :
- (A) 3.17 (B) 0.317 (C) 317 (D) 31.7
14. A current of 9.65 amp. passing for 16 min. 40 sec. through a molten tin salt deposits 5.95 g. of tin The oxidation state of the tin in the salt is : (at. wt of Sn = 119)
- (A) +4 (B) +3 (C) +2 (D) +1
15. The time required for a current of 3 amp. to decompose electrolytically 18 g of  $\text{H}_2\text{O}$  is:
- (A) 18 hour (B) 36 hour (C) 9 hour (D) 18 seconds
16. An ion is reduced to the element when it absorbs  $6 \times 10^{20}$  electrons. The number of gm equivalents of the ion is :
- (A) 0.10 (B) 0.01 (C) 0.001 (D) 0.0001
17. How many coulombs of electric charge are required for the oxidation of 1 mole of  $\text{H}_2\text{O}$  to  $\text{O}_2$  ?
- (A)  $9.65 \times 10^4 \text{ C}$  (B)  $4.825 \times 10^5 \text{ C}$  (C)  $1.93 \times 10^5 \text{ C}$  (D)  $1.93 \times 10^4 \text{ C}$
18. The time required to coat a meter surface of  $80 \text{ cm}^2$  with  $5 \times 10^{-3} \text{ cm}$  thick layer of silver (density  $1.08 \text{ g cm}^{-3}$ ) with the passage of 9.65A current through a silver nitrate solution is :
- (A) 10 sec. (B) 40 sec. (C) 30 sec. (D) 20 sec.
19. One gm metal  $\text{M}^{+2}$  was discharged by the passage of  $1.2 \times 10^{22}$  electrons. What is the atomic weight of metal?
- (A) 25 (B) 50 (C) 100 (D) 75

20. One mole of electron passes through each of the solution of  $\text{AgNO}_3$ ,  $\text{CuSO}_4$  and  $\text{AlCl}_3$  when Ag, Cu and Al are deposited at cathode. The molar ratio of Ag, Cu and Al deposited are  
(A) 1 : 1 : 1                      (B) 6 : 3 : 2                      (C) 6 : 3 : 1                      (D) 1 : 3 : 6
21. During electrolysis of an aqueous solution of sodium sulphate, 2.4 L of oxygen at STP was liberated at anode. The volume of hydrogen at STP, liberated at cathode would be  
(A) 1.2 L                      (B) 2.4 L                      (C) 2.6 L                      (D) 4.8 L
22. The charge required for the oxidation of one mole  $\text{Mn}_3\text{O}_4$  into  $\text{MnO}_4^{2-}$  in presence of alkaline medium is  
(A)  $5 \times 96500 \text{ C}$                       (B)  $96500 \text{ C}$                       (C)  $10 \times 96500 \text{ C}$                       (D)  $2 \times 96500 \text{ C}$

**CONDUCTANCE**

23. Equivalent conductances of  $\text{Ba}^{+2}$  and  $\text{Cl}^-$  ions are 127 &  $76 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$  respectively. Equivalent conductance of  $\text{BaCl}_2$  at infinite dilution is -  
(A) 379                      (B) 139.5                      (C) 203                      (D) 330
24. If x is specific resistance of the electrolyte solution and y is the molarity of the solution, then  $\Lambda_m$  is given by  
(A)  $\frac{1000x}{y}$                       (B)  $1000 \frac{y}{x}$                       (C)  $\frac{1000}{xy}$                       (D)  $\frac{xy}{1000}$

## EXERCISE (O-II)

## Single correct :

- Consider the reaction,  

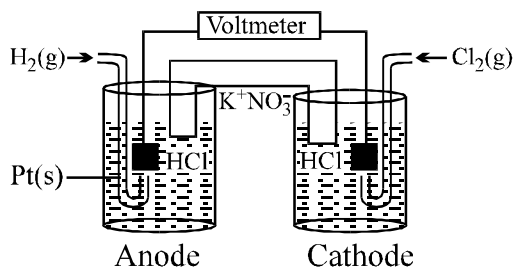
$$\text{Cl}_{2(g)} + 2\text{Br}^-_{(aq)} \longrightarrow 2\text{Cl}^-_{(aq)} + \text{Br}_{2(g)}$$
 The emf of the cell when  $[\text{Cl}^-] = [\text{Br}^-] = 0.01\text{M}$  and  $\text{Cl}_2$  gas at 1 atm pressure while  $\text{Br}_2(g)$  at 0.01 atm will be ( $E^\circ$  for the above reaction is = 0.29 volt) :  
 (A) 0.54 volt (B) 0.35 volt (C) 0.24 volt (D) -0.29 volt
- How much will the reduction potential of a hydrogen electrode change when its solution initially at pH = 0 is neutralised to pH = 7 ?  
 (A) increase by 0.059V (B) decrease by 0.059V  
 (C) increase by 0.413V (D) decrease by 0.413V
- If the pressure of  $\text{H}_2$  gas is increased from 1 atm to 100 atm keeping  $\text{H}^+$  concentration constant at 1 M, the change in reduction potential of hydrogen half cell at  $25^\circ\text{C}$  will be  
 (A) 0.059 V (B) 0.59 V (C) 0.0295 V (D) 0.118 V
- A silver wire dipped in 0.1 M HCl solution saturated with AgCl develops oxidation potential of -0.209 V. If  $E^\circ_{\text{Ag}/\text{Ag}^+} = -0.799\text{ V}$ , the  $K_{\text{sp}}$  of AgCl in pure water will be  
 (A)  $3 \times 10^{-11}$  (B)  $10^{-11}$  (C)  $4 \times 10^{-11}$  (D)  $3 \times 10^{-11}$
- Salts of A (atomic weight = 7), B (atomic weight = 27) and C (atomic weight = 48) were electrolysed under identical conditions using the same quantity of electricity. It was found that when 2.1 g of A was deposited, the weights of B and C deposited were 2.7 and 7.2 g. The valencies of A, B and C respectively are  
 (A) 3, 1 and 2 (B) 1, 3 and 2 (C) 3, 1 and 3 (D) 2, 3 and 2
- During electro refining of Cu by electrolysis of an aqueous solution of  $\text{CuSO}_4$  using copper electrodes, if 2.5 g of Cu is deposited at cathode, then at anode  
 (A) decrease of more than 2.5 g of mass takes place  
 (B) 450 ml of  $\text{O}_2$  at STP is liberated  
 (C) 2.5 g of copper is deposited  
 (D) a decrease of 2.5 g of mass takes place
- The conductivity of a saturated solution of  $\text{Ag}_3\text{PO}_4$  is  $9 \times 10^{-6}\text{ S m}^{-1}$  and its equivalent conductivity is  $1.50 \times 10^{-4}\text{ S m}^2\text{ equivalent}^{-1}$ . The  $K_{\text{sp}}$  of  $\text{Ag}_3\text{PO}_4$  is  
 (A)  $4.32 \times 10^{-18}$  (B)  $1.8 \times 10^{-9}$  (C)  $8.64 \times 10^{-13}$  (D) None of these
- Equal volumes of 0.015 M  $\text{CH}_3\text{COOH}$  & 0.015 M NaOH are mixed together. What would be molar conductivity of mixture if conductivity of  $\text{CH}_3\text{COONa}$  is  $6.3 \times 10^{-4}\text{ S cm}^{-1}$   
 (A)  $8.4\text{ S cm}^2\text{ mol}^{-1}$  (B)  $84\text{ S cm}^2\text{ mol}^{-1}$  (C)  $4.2\text{ S cm}^2\text{ mol}^{-1}$  (D)  $42\text{ S cm}^2\text{ mol}^{-1}$
- For the fuel cell reaction  $2\text{H}_2(g) + \text{O}_2(g) \longrightarrow 2\text{H}_2\text{O}(l)$ ;  $\Delta_f H^\circ_{298}(\text{H}_2\text{O}, l) = -285.5\text{ kJ/mol}$

What is  $\Delta S^\circ_{298}$  for the given fuel cell reaction?

Given:  $\text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \longrightarrow 2\text{H}_2\text{O}(l)$   $E^\circ = 1.23\text{ V}$

- (A)  $-0.322\text{ J/K}$  (B)  $-0.635\text{ kJ/K}$  (C)  $3.51\text{ kJ/K}$  (D)  $-0.322\text{ kJ/K}$

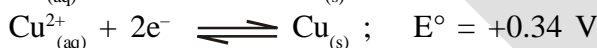
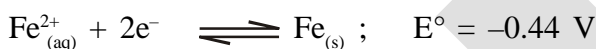
10. Consider the following Galvanic cell.



By what value the cell voltage change when concentration of ions in anodic and cathodic compartments both increased by factor of 10 at 298 K

- (A) +0.0590 (B) -0.0590 (C) -0.1180 (D) 0
11. The standard reduction potentials at 25°C for the following half reactions are :
- $$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Zn}(\text{s}), E_{\text{RP}}^\circ = -0.762\text{V}$$
- $$\text{Cr}^{3+}(\text{aq}) + 3\text{e}^- \rightleftharpoons \text{Cr}(\text{s}), E_{\text{RP}}^\circ = -0.740\text{V}$$
- $$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g}), E_{\text{RP}}^\circ = 0.00\text{V}$$
- $$\text{Fe}^{3+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Fe}^{2+}(\text{aq}), E_{\text{RP}}^\circ = 0.77\text{V}$$
- Which is the strongest reducing agent ?

- (A) Zn (B) Cr (C)  $\text{H}_2(\text{g})$  (D)  $\text{Fe}^{2+}(\text{aq})$
12. Using the standard electrode potential values given below, decide which of the statements, I, II, III and IV are correct. Choose the right answer from (A), (B), (C) and (D).



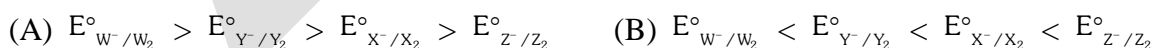
I. Copper can displace iron from  $\text{FeSO}_4$  solution.

II. Iron can displace copper from  $\text{CuSO}_4$  solution.

III. Silver can displace copper from  $\text{CuSO}_4$  solution.

IV. Iron can displace silver from  $\text{AgNO}_3$  solution.

- (A) I and II (B) II and III (C) II and IV (D) I and IV
13. The following facts are available :-
- $$2\text{X}^- + \text{Y}_2 \rightarrow 2\text{Y}^- + \text{X}_2$$
- $$2\text{W}^- + \text{Y}_2 \rightarrow \text{NO reaction}$$
- $$2\text{Z}^- + \text{X}_2 \rightarrow 2\text{X}^- + \text{Z}_2$$
- Which of the following statements is correct :-



14. The cost of electricity required to deposit 1 g of Mg is Rs. 5.00. How much would it cost to deposit 9 g of Al (At wt. Al = 27, Mg = 24)
- (A) Rs. 10 (B) Rs. 27 (C) Rs. 40 (D) Rs. 60
15. 4.5g of aluminium (at. mass 27 amu) is deposited at cathode from  $\text{Al}^{3+}$  solution by a certain quantity of electric charge. The volume of hydrogen produced at STP from  $\text{H}^+$  ions in solution by the same quantity of electric charge will be -
- (A) 45.4L (B) 11.35L (C) 22.7L (D) 5.675 L



- (A)  $\text{Cl}_2$  can oxidise  $\text{SO}_4^{2-}$  from solution  
 (B)  $\text{Cl}_2$  can oxidise  $\text{Br}^-$  and  $\text{I}^-$  from aqueous solution  
 (C)  $\text{S}_2\text{O}_8^{2-}$  can oxidise  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  from aqueous solution  
 (D)  $\text{S}_2\text{O}_8^{2-}$  is added slowly,  $\text{Br}^-$  can be reduce in presence of  $\text{Cl}^-$
24. The EMF of the following cell is 0.22 volt.  
 $\text{Ag(s)} \mid \text{AgCl(s)} \mid \text{KCl (1M)} \mid \text{H}^+(1\text{M}) \mid \text{H}_2(\text{g}) (1\text{ atm}) \mid \text{Pt(s)}.$   
 Which of the following will decrease the EMF of cell.  
 (A) increasing pressure of  $\text{H}_2(\text{g})$  from 1 atm to 2 atm  
 (B) increasing  $\text{Cl}^-$  concentration in Anodic compartment  
 (C) increasing  $\text{H}^+$  concentration in cathodic compartment  
 (D) decreasing  $\text{KCl}$  concentration in Anodic compartment.

**Assertion & Reasoning type questions :**

25. Statement -1 : The voltage of mercury cell remains constant for long period of time.  
 Statement -2 : It is because net cell reaction does not involve active species.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.
26. Statement -1 : The SRP of three metallic ions  $\text{A}^+$ ,  $\text{B}^{2+}$ ,  $\text{C}^{3+}$  are  $-0.3$ ,  $-0.5$ ,  $0.8$  volt respectively, so oxidising power of ions is  $\text{C}^{3+} > \text{A}^+ > \text{B}^{2+}$ .  
 Statement -2 : Higher the SRP, higher the oxidising power.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.
27. Statement -1 : We can add the electrode potential in order to get electrode potential of net reaction.  
 Statement -2 : Electrode potential is an intensive property.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

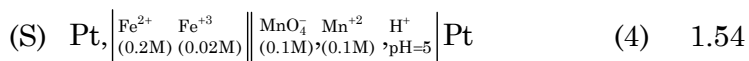
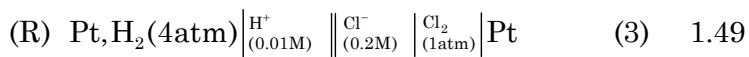


32. Column-I

Column-II

Cell notation :

$E_{\text{cell}}$



Given :

$$E_{\text{Cu}^{2+}/\text{Cu}}^0 = 0.34\text{V}$$

$$K_{\text{sp}}(\text{AgBr}) = 10^{-13}$$

$$E_{\text{Mn}^{2+}/\text{Mn}}^0 = -1.18\text{V}$$

$$\frac{2.303RT}{F} = 0.06$$

$$E_{\text{Ag}^+/\text{Ag}}^0 = 0.8\text{V}$$

$$E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 = 0.77\text{V}$$

$$E_{\text{MnO}_4^-/\text{Mn}^{2+}}^0 = 1.52\text{V}$$

$$E_{\text{Cl}_2/\text{Cl}^-}^0 = 1.36\text{V}$$

Code:

|     | P | Q | R | S |
|-----|---|---|---|---|
| (A) | 4 | 3 | 4 | 4 |
| (B) | 2 | 3 | 1 | 4 |
| (C) | 3 | 2 | 4 | 1 |
| (D) | 4 | 3 | 2 | 1 |



## EXERCISE (J-MAINS)

- Resistance of 0.2 M solution of an electrolyte is  $50 \Omega$ . The specific conductance of the solution is  $1.3 \text{ S m}^{-1}$ . If resistance of the 0.4M solution of the same electrolyte is  $260 \Omega$ , its molar conductivity is :- **[AIEEE 2011]**  
 (1)  $6250 \text{ S m}^2 \text{ mol}^{-1}$  (2)  $6.25 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$   
 (3)  $625 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$  (4)  $62.5 \text{ S m}^2 \text{ mol}^{-1}$
- The reduction potential of hydrogen half-cell will be negative if :- **[AIEEE 2011]**  
 (1)  $p(\text{H}_2) = 2 \text{ atm}$   $[\text{H}^+] = 1.0 \text{ M}$  (2)  $p(\text{H}_2) = 2 \text{ atm}$  and  $[\text{H}^+] = 2.0 \text{ M}$   
 (3)  $p(\text{H}_2) = 1 \text{ atm}$  and  $[\text{H}^+] = 2.0 \text{ M}$  (4)  $p(\text{H}_2) = 1 \text{ atm}$  and  $[\text{H}^+] = 1.0 \text{ M}$
- The standard reduction potentials for  $\text{Zn}^{2+} | \text{Zn}$ ,  $\text{Ni}^{2+} | \text{Ni}$  and  $\text{Fe}^{2+} | \text{Fe}$  are  $-0.76$ ,  $-0.23$  and  $-0.44 \text{ V}$  respectively. The reaction  $\text{X} + \text{Y}^{2+} \rightarrow \text{X}^{2+} + \text{Y}$  will be spontaneous when **[AIEEE 2012]**  
 (1)  $\text{X} = \text{Zn}$ ,  $\text{Y} = \text{Ni}$  (2)  $\text{X} = \text{Ni}$ ,  $\text{Y} = \text{Fe}$  (3)  $\text{X} = \text{Ni}$ ,  $\text{Y} = \text{Zn}$  (4)  $\text{X} = \text{Fe}$ ,  $\text{Y} = \text{Zn}$
- Given : **[JEE-MAINS 2013]**  

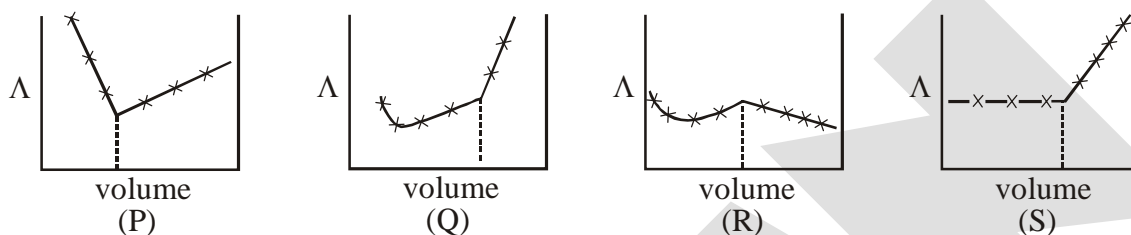
$$E_{\text{Cr}^{3+}/\text{Cr}}^0 = -0.74 \text{ V} ; E_{\text{MnO}_4^-/\text{Mn}^{2+}}^0 = 1.51 \text{ V}$$

$$E_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}}^0 = 1.33 \text{ V} ; E_{\text{Cl}_2/\text{Cl}^-}^0 = 1.36 \text{ V}$$
 Based on the data given above, strongest oxidising agent will be :  
 (1)  $\text{Cl}^-$  (2)  $\text{Cr}^{3+}$  (3)  $\text{Mn}^{2+}$  (4)  $\text{MnO}_4^-$
- The equivalent conductance of  $\text{NaCl}$  at concentration  $C$  and at infinite dilution are  $\lambda_C$  and  $\lambda_\infty$ , respectively. The correct relationship between  $\lambda_C$  and  $\lambda_\infty$  is given as : **[JEE-MAINS 2014]**  
 (where the constant  $B$  is positive)  
 (1)  $\lambda_C = \lambda_\infty - (2) \sqrt{C}$  (2)  $\lambda_C = \lambda_\infty + (2) \sqrt{C}$   
 (3)  $\lambda_C = \lambda_\infty + (2) C$  (4)  $\lambda_C = \lambda_\infty - (2) C$
- Resistance of 0.2 M solution of an electrolyte is  $50 \Omega$ . The specific conductance of the solution is  $1.4 \text{ S m}^{-1}$ . The resistance of 0.5 M solution of the same electrolyte is  $280 \Omega$ . The molar conductivity of 0.5 M solution of the electrolyte in  $\text{S m}^2 \text{ mol}^{-1}$  is : **[JEE-MAINS 2014]**  
 (1)  $5 \times 10^3$  (2)  $5 \times 10^2$  (3)  $5 \times 10^{-4}$  (4)  $5 \times 10^{-3}$
- At  $298 \text{ K}$ , the standard reduction potentials are  $1.51 \text{ V}$  for  $\text{MnO}_4^- | \text{Mn}^{2+}$ ,  $1.36 \text{ V}$  for  $\text{Cl}_2 | \text{Cl}^-$ ,  $1.07 \text{ V}$  for  $\text{Br}_2 | \text{Br}^-$ , and  $0.54 \text{ V}$  for  $\text{I}_2 | \text{I}^-$ . At  $\text{pH} = 3$ , permanganate is expected to oxidize  $\left(\frac{RT}{F} = 0.059 \text{ V}\right)$  :- **[JEE-MAINS (ONLINE) 2015]**  
 (1)  $\text{Cl}^-$  and  $\text{Br}^-$  (2)  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  (3)  $\text{Br}^-$  and  $\text{I}^-$  (4)  $\text{I}^-$  only
- A variable, opposite external potential ( $E_{\text{ext}}$ ) is applied to the cell  $\text{Zn} | \text{Zn}^{2+} (1 \text{ M}) || \text{Cu}^{2+} (1 \text{ M}) | \text{Cu}$ , of potential  $1.1 \text{ V}$ . When  $E_{\text{ext}} < 1.1 \text{ V}$  and  $E_{\text{ext}} > 1.1 \text{ V}$ , respectively electrons flow from : **[JEE-MAINS (ONLINE) 2015]**  
 (1) anode to cathode in both cases  
 (2) anode to cathode and cathode to anode  
 (3) cathode to anode in both cases  
 (4) cathode to anode and anode to cathode

9. Two Faraday of electricity is passed through a solution of  $\text{CuSO}_4$ . The mass of copper deposited at the cathode is : (at. mass of Cu = 63.5 amu) [JEE-MAINS 2015]  
 (1) 2g (2) 127 g (3) 0 g (4) 63.5 g
10. What will occur if a block of copper metal is dropped into a beaker containing a solution of 1M  $\text{ZnSO}_4$   
 (1) The copper metal will dissolve and zinc metal will be deposited  
 (2) No reaction will occur [JEE-MAINS (ONLINE) 2016]  
 (3) The copper metal will dissolve with evolution of oxygen gas  
 (4) The copper metal will dissolve with evolution of hydrogen gas
11. Oxidation of succinate ion produces ethylene and carbon dioxide gases. On passing 0.2 Faraday electricity through on aqueous solution of potassium succinate, the total volume of gases (at both cathode and anode) at STP (1 atm and 273 K) is : [JEE-MAINS (ONLINE) 2016]  
 (1) 8.96 L (2) 2.24 L (3) 4.48 L (4) 6.72 L
12. Given [JEE-MAINS - 2017]  
 $E^\circ_{\text{Cl}_2/\text{Cl}^-} = 1.36 \text{ V}$ ,  $E^\circ_{\text{Cr}^{3+}/\text{Cr}} = -0.74 \text{ V}$   
 $E^\circ_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}} = 1.33 \text{ V}$ ,  $E^\circ_{\text{MnO}_4^-/\text{Mn}^{2+}} = 1.51 \text{ V}$ .  
 Among the following, the strongest reducing agent is  
 (1) Cr (2)  $\text{Mn}^{2+}$  (3)  $\text{Cr}^{3+}$  (4)  $\text{Cl}^-$
13. What is the standard reduction potential ( $E^\circ$ ) for  $\text{Fe}^{3+} \rightarrow \text{Fe}$  ? [JEE-MAINS (ONLINE) 2017]  
 Given that :  
 $\text{Fe}^{2+} + 2e^- \rightarrow \text{Fe}$  ;  $E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.47 \text{ V}$   
 $\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$  ;  $E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = +0.77 \text{ V}$   
 (1) +0.30 V (2) +0.057 V (3) -0.057 V (4) -0.30 V
14. To find the standard potential of  $\text{M}^{3+}|\text{M}$  electrode, the following cell is constituted:  $\text{Pt}|\text{M}|\text{M}^{3+}(0.001 \text{ mol L}^{-1})|\text{Ag}^+(0.01 \text{ mol L}^{-1})|\text{Ag}$  [JEE-MAINS (ONLINE) 2017]  
 The emf of the cell is found to be 0.421 volt at 298 K. The standard potential of half reaction  $\text{M}^{3+} + 3e^- \rightarrow \text{M}$  at 298 K will be : (Given  $E^\circ_{\text{Ag}^+/\text{Ag}} = 0.80 \text{ Volt}$ )  
 (1) +0.30 V (2) +0.057 V (3) -0.057 V (4) -0.30 V
15. How long (approximate) should water be electrolysed by passing through 100 amperes current so that the oxygen released can completely burn 27.66 g of diborane ? [JEE-MAINS (OFFLINE) 2017]  
 (Atomic weight of B = 10.8 u)  
 (1) 0.8 hours (2) 3.2 hours (3) 1.6 hours (4) 6.4 hours
16. When an electric current is passed through acidified water, 112 mL of hydrogen gas at N.T.P. was collected at the catode in 965 seconds. The current passed, in ampere, is : [JEE-MAINS (ONLINE) 2018]  
 (1) 2.0 (2) 1.0 (3) 0.1 (4) 0.5
17. When 9.65 ampere current was passed for 1.0 hour into nitrobenzene in acidic medium, the amount of p-aminophenol produced is :- [JEE-MAINS (ONLINE) 2018]  
 (1) 10.9 g (2) 98.1 g (3) 109.0 g (4) 9.81 g

## EXERCISE (J-ADVANCED)

1. Consider the following cell reaction : [JEE 2011]  
 $2\text{Fe}_{(s)} + \text{O}_{2(g)} + 4\text{H}^+_{(aq)} \rightarrow 2\text{Fe}^{2+}_{(aq)} + 2\text{H}_2\text{O}(\ell) \quad E^\circ = 1.67 \text{ V}$   
 At  $[\text{Fe}^{2+}] = 10^{-3} \text{ M}$ ,  $P(\text{O}_2) = 0.1 \text{ atm}$  and  $\text{pH} = 3$ , the cell potential at  $25^\circ\text{C}$  is -  
 (A) 1.47 V (B) 1.77 V (C) 1.87 V (D) 1.57 V
2.  $\text{AgNO}_3$  (a) was added to an aqueous KCl solution gradually and the conductivity of the solution was measured. the plot of conductance ( $\Lambda$ ) versus the volume of  $\text{AgNO}_3$  is - [JEE 2011]



- (A) (P) (B) (Q) (C) (R) (D) (S)

**Paragraph for Question 3 and 4**

The electrochemical cell shown below is a concentration cell.

[JEE 2012]

$\text{M} | \text{M}^{2+}$  (saturated solution of a sparingly soluble salt,  $\text{MX}_2$ )  $||$   $\text{M}^{2+}$  ( $0.001 \text{ mol dm}^{-3}$ )  $| \text{M}$

The emf of the cell depends on the difference in concentrations of  $\text{M}^{2+}$  ions at the two electrodes. The emf of the cell at  $298 \text{ K}$  is  $0.059 \text{ V}$ .

3. The value of  $\Delta G$  ( $\text{kJ mol}^{-1}$ ) for the given cell is (take  $F = 96500 \text{ C mol}^{-1}$ )  
 (A)  $-5.7$  (B)  $5.7$  (C)  $11.4$  (D)  $-11.4$ .
4. The solubility product ( $K_{\text{sp}}$ ;  $\text{mol}^3 \text{ dm}^{-9}$ ) of  $\text{MX}_2$  at  $298 \text{ K}$  based on the information available for the given concentration cell is (take  $2.303 \times R \times 298 / F = 0.059 \text{ V}$ )  
 (A)  $1 \times 10^{-15}$  (B)  $4 \times 10^{-15}$  (C)  $1 \times 10^{-12}$  (D)  $1 \times 10^{-12}$
5. The standard reduction potential data at  $25^\circ\text{C}$  is given below [JEE-Adv. 2013]

$$E^\circ (\text{Fe}^{3+}, \text{Fe}^{2+}) = +0.77 \text{ V} ;$$

$$E^\circ (\text{Fe}^{2+}, \text{Fe}) = -0.44 \text{ V} ;$$

$$E^\circ (\text{Cu}^{2+}, \text{Cu}) = +0.34 \text{ V} ;$$

$$E^\circ (\text{Cu}^+, \text{Cu}) = +0.52 \text{ V} ;$$

$$E^\circ (\text{O}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}) = +1.23 \text{ V} ;$$

$$E^\circ [(\text{O}_2(\text{g}) + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-)] = +0.40 \text{ V} ;$$

$$E^\circ (\text{Cr}^{3+}, \text{Cr}) = -0.74 \text{ V} ;$$

$$E^\circ (\text{Cr}^{2+}, \text{Cr}) = -0.91 \text{ V} ;$$

Match  $E^\circ$  of the redox pair in List-I with the values given in List-II and select the correct answer using the code given below the lists :

| List-I |                                                                              | List-II |                   |
|--------|------------------------------------------------------------------------------|---------|-------------------|
| (P)    | $E^\circ(\text{Fe}^{3+}, \text{Fe})$                                         | (1)     | $-0.18 \text{ V}$ |
| (Q)    | $E^\circ(4\text{H}_2\text{O} \rightleftharpoons 4\text{H}^+ + 4\text{OH}^-)$ | (2)     | $-0.4 \text{ V}$  |
| (R)    | $E^\circ(\text{Cu}^{2+} + \text{Cu} \rightarrow 2\text{Cu}^+)$               | (3)     | $-0.04 \text{ V}$ |
| (S)    | $E^\circ(\text{Cr}^{3+}, \text{Cr}^{2+})$                                    | (4)     | $-0.83 \text{ V}$ |

Codes :

|     | P | Q | R | S |     | P | Q | R | S |
|-----|---|---|---|---|-----|---|---|---|---|
| (A) | 4 | 1 | 2 | 3 | (B) | 2 | 3 | 4 | 1 |
| (C) | 1 | 2 | 3 | 4 | (D) | 3 | 4 | 1 | 2 |

6. An aqueous solution of X is added slowly to an aqueous solution of Y as shown in List-I. The variation in conductivity of these reactions is given in List-II. Match List-I with List-II and select the correct answer using the code given below the lists : [JEE-Adv. 2013]

| List-I |                                                                                     | List-II |                                                      |
|--------|-------------------------------------------------------------------------------------|---------|------------------------------------------------------|
| (P)    | $(\text{C}_2\text{H}_5)_3\text{N} + \text{CH}_3\text{COOH}$<br>X                  Y | (1)     | Conductivity decreases and then increases            |
| (Q)    | $\text{KI}(0.1\text{M}) + \text{AgNO}_3(0.01\text{M})$<br>X                  Y      | (2)     | Conductivity decreases and then does not change much |
| (R)    | $\text{CH}_3\text{COOH} + \text{KOH}$<br>X                  Y                       | (3)     | Conductivity increases and then does not change much |
| (S)    | $\text{NaOH} + \text{HI}$<br>X                  Y                                   | (4)     | Conductivity does not change much and then increases |

Codes :

|     | P | Q | R | S |     | P | Q | R | S |
|-----|---|---|---|---|-----|---|---|---|---|
| (A) | 3 | 4 | 2 | 1 | (B) | 4 | 3 | 2 | 1 |
| (C) | 2 | 3 | 4 | 1 | (D) | 1 | 4 | 3 | 2 |

7. In a galvanic cell, the salt bridge - [JEE-Adv. 2014]  
 (A) Does not participate chemically in the cell reaction  
 (B) Stops the diffusion of ions from one electrode to another  
 (C) Is necessary for the occurrence of the cell reaction  
 (D) Ensures mixing of the two electrolytic solutions
8. The molar conductivity of a solution of a weak acid HX (0.01 M) is 10 times smaller than the molar conductivity of a solution of a weak acid HY (0.1 M). If  $\lambda_{\text{X}^-}^0 \approx \lambda_{\text{Y}^-}^0$ , the difference in their  $\text{pK}_a$  values,  $\text{pK}_a(\text{HX}) - \text{pK}_a(\text{HY})$ , is (consider degree of ionization of both acids to be  $\ll 1$ ). [JEE-Adv. 2015]
9. All the energy released from the reaction  $\text{X} \rightarrow \text{Y}$ ,  $\Delta_r G^\circ = -193 \text{ kJ mol}^{-1}$  is used for the oxidizing  $\text{M}^+$  and  $\text{M}^+ \rightarrow \text{M}^{3+} + 2\text{e}^-$ ,  $E^\circ = -0.25 \text{ V}$ . [JEE-Adv. 2015]  
 Under standard conditions, the number of moles of  $\text{M}^+$  oxidized when one mole of X is converted to Y is -  $[F = 96500 \text{ C mol}^{-1}]$

10. For the following electrochemical cell at 298K, [JEE-Adv. 2016]  
 $\text{Pt(s)} \mid \text{H}_2(\text{g}, 1\text{bar}) \mid \text{H}^+(\text{aq}, 1\text{M}) \parallel \text{M}^{4+}(\text{aq}), \text{M}^{2+}(\text{aq}) \mid \text{Pt(s)}$   
 $E_{\text{cell}} = 0.092 \text{ V}$  when  $\frac{[\text{M}^{2+}(\text{aq})]}{[\text{M}^{4+}(\text{aq})]} = 10^x$   
 Given :  $E_{\text{M}^{4+}/\text{M}^{2+}}^0 = 0.151 \text{ V}$  ;  $2.303 \frac{RT}{F} = 0.059 \text{ V}$   
 The value of  $x$  is -  
 (A) -2 (B) -1 (C) 1 (D) 2
11. The conductance of a 0.0015 M aqueous solution of a weak monobasic acid was determined by using a conductivity cell consisting of platinized Pt electrodes. The distance between the electrodes is 120 cm with an area of cross section of  $1 \text{ cm}^2$ . The conductance of this solution was found to be  $5 \times 10^{-7} \text{ S}$ . The pH of the solution is 4. The value of limiting molar conductivity ( $\Lambda_m^0$ ) of this weak monobasic acid in aqueous solution is  $Z \times 10^2 \text{ S cm}^{-1} \text{ mol}^{-1}$ . The value of  $Z$  is.
12. For the following cell : [JEE-Adv. 2017]  
 $\text{Zn(s)} \mid \text{ZnSO}_4(\text{aq.}) \parallel \text{CuSO}_4(\text{aq.}) \mid \text{Cu(s)}$   
 when the concentration of  $\text{Zn}^{2+}$  is 10 times the concentration of  $\text{Cu}^{2+}$ , the expression for  $\Delta G$  (in  $\text{J mol}^{-1}$ ) is  
 [F is Faraday constant, R is gas constant, T is temperature,  $E^0(\text{cell}) = 1.1 \text{ V}$ ]  
 (A)  $2.303 RT + 1.1F$  (B)  $2.303 RT - 2.2F$   
 (C)  $1.1 F$  (D)  $-2.2 F$
13. Consider an electrochemical cell:  $\text{A(s)} \mid \text{A}^{n+}(\text{aq}, 2\text{M}) \parallel \text{B}^{2n+}(\text{aq}, 1\text{M}) \mid \text{B(s)}$ . The value of  $\Delta H^0$  for the cell reaction is twice that of  $\Delta G^0$  at 300 K. If the emf of the cell is zero, the  $\Delta S^0$  (in  $\text{JK}^{-1} \text{ mol}^{-1}$ ) of the cell reaction per mole of B formed at 300 K is \_\_\_\_\_. [JEE-Adv. 2018]  
 (Given :  $\ln(2) = 0.7$ , R (universal gas constant) =  $8.3 \text{ J K}^{-1} \text{ mol}^{-1}$ . H, S and G are enthalpy, entropy and Gibbs energy, respectively.)
14. For the electrochemical cell,  
 $\text{Mg(s)} \mid \text{Mg}^{2+}(\text{aq}, 1\text{M}) \parallel \text{Cu}^{2+}(\text{aq}, 1\text{M}) \mid \text{Cu(s)}$   
 the standard emf of the cell is 2.70 V at 300 K. When the concentration of  $\text{Mg}^{2+}$  is changed to  $x \text{ M}$ , the cell potential changes to 2.67 V at 300 K. The value of  $x$  is \_\_\_\_\_. [JEE-Adv. 2018]  
 (Given,  $\frac{F}{R} = 11500 \text{ KV}^{-1}$ , where F is the Faraday constant and R is the gas constant,  $\ln(10) = 2.30$ )

# ANSWER KEY

## EXERCISE (S-I)

1. Ans. 0.53 V, disproportionation
2. Ans.  $K_c = 2.868 \times 10^{107}$ ,  $\Delta G^0 = -611.8 \text{ kJ}$
3. Ans.  $E^0 = -0.14903 \text{ V}$
4. Ans.  $E = -0.81 \text{ V}$
5. Ans.  $K_w \approx 10^{-14}$
6. Ans.  $-1.30 \times 10^3 \text{ kJ mol}^{-1}$
7. Ans. 3.86
8. Ans. (3)
9. Ans.  $E = 0.059$
10. Ans.  $E = 0.413 \text{ V}$
11. Ans.  $1.023 \times 10^5 \text{ sec}$
12. Ans. 115800C, 347.4 kJ
13. Ans. 1.12 mol, 12.535 litre
14. Ans. Rs. 0.75 x
15. Ans.  $A = 114$ ,  $Q = 5926.8 \text{ C}$
16. Ans. 60 %
17. Ans. 1.825g
18. Ans. 2M
19. Ans. (i)  $250 \text{ mho cm}^2 \text{ mol}^{-1}$ , (ii)  $125 \text{ mho cm}^2 \text{ equivalent}^{-1}$
20. Ans.  $9.4 \times 10^{-4} \text{ gm/litre}$
21. Ans.  $\alpha = 0.5$ ,  $k = 10 \times 10^{-4}$
22. Ans. (i) 7 (ii)  $1 \times 10^{-14}$

## EXERCISE (S-II)

1. Ans. -0.46 V
2. Ans. (ii). 1.27 V, (iii) 245.1 kJ
3. Ans.  $E^0 = -0.22 \text{ V}$
4. Ans.  $K_{sp} = 1.1 \times 10^{-16}$
5. Ans.  $[\text{Br}^-] : [\text{Cl}^-] = 1 : 200$
6. Ans. -0.037 V
7. Ans.  $1.536 \times 10^{-5} \text{ M}^3$
8. Ans.  $K = 10^{268}$
9. Ans. 43.456g
10. Ans. 42.2 %
11. Ans.  $1.9 \times 10^6 \text{ year}$
12. Ans. 0.1456 ampere
13.  $4.25 \times 10^{-2} \text{ metre}$
14. Ans. 0.1934 gm/litre
15. Ans.  $n = 2$
16. Ans. 0.52 V, 0.61 V
17. Ans. 0.0295 V
18. Ans.  $t = 193 \text{ sec}$
19. Ans. Final weight = 9.6g, 0.01 Eq of acid
20. Ans.  $t = 93.65 \text{ sec}$ .

## EXERCISE (O-I)

- |            |            |            |            |
|------------|------------|------------|------------|
| 1. Ans. C  | 2. Ans. A  | 3. Ans. C  | 4. Ans. A  |
| 5. Ans. C  | 6. Ans. C  | 7. Ans. A  | 8. Ans. B  |
| 9. Ans. D  | 10. Ans. B | 11. Ans. B | 12. Ans. D |
| 13. Ans. D | 14. Ans. C | 15. Ans. A | 16. Ans. C |
| 17. Ans. C | 18. Ans. B | 19. Ans. C | 20. Ans. B |
| 21. Ans. D | 22. Ans. C | 23. Ans. C | 24. Ans. C |

**EXERCISE (O-II)**

- |               |             |                                              |              |
|---------------|-------------|----------------------------------------------|--------------|
| 1. Ans.B      | 2. Ans.D    | 3. Ans.A                                     | 4. Ans.B     |
| 5. Ans. B     | 6. Ans.A    | 7. Ans.A                                     | 8. Ans.B     |
| 9. Ans.D      | 10. Ans.C   | 11. Ans. A                                   | 12. Ans.C    |
| 13. Ans.(B)   | 14. Ans.D   | 15. Ans.D                                    | 16. Ans.B    |
| 17. Ans.C     | 18. Ans.C   | 19. Ans.C                                    | 20. Ans. C,D |
| 21. Ans.B,C,D | 22. Ans.A,B | 23. Ans.B,C                                  | 24. Ans.A,D  |
| 25. Ans.A     | 26. Ans.A   | 27. Ans.D                                    | 28. Ans.(C)  |
| 29. Ans.(A)   | 30. Ans.(C) | 31. Ans. (A) P, Q (B) P, Q (C) Q, R, (D) P,S |              |
| 32. Ans.(C)   |             |                                              |              |

**EXERCISE (J-MAINS)**

- |             |             |              |              |
|-------------|-------------|--------------|--------------|
| 1. Ans.(2)  | 2. Ans.(1)  | 3. Ans.(1)   | 4. Ans.(4)   |
| 5. Ans. (1) | 6. Ans.(3)  | 7. Ans. (3)  | 8. Ans. (2)  |
| 9. Ans.(4)  | 10. Ans.(2) | 11. Ans. (1) | 12. Ans. (1) |
| 13. Ans.(3) | 14. Ans.(2) | 15. Ans.(2)  | 16. Ans.(2)  |
| 17. Ans.(4) |             |              |              |

**EXERCISE (J-ADVANCED)**

- |                  |              |              |             |
|------------------|--------------|--------------|-------------|
| 1. Ans.(D)       | 2. Ans.(D)   | 3. Ans.(D)   | 4. Ans.(B)  |
| 5. Ans.(D)       | 6. Ans.(A)   | 7. Ans.(A,B) | 8. Ans. (3) |
| 9. Ans. (4)      | 10. Ans.(D)  | 11. Ans.(6)  | 12. Ans.(B) |
| 13. Ans.(-11.62) | 14. Ans.(10) |              |             |

**NURTURE COURSE**

**ELECTRONIC DISPLACEMENT EFFECTS**

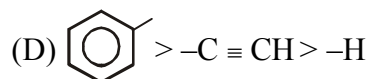
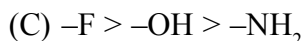
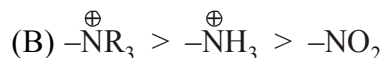
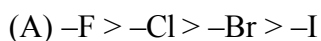




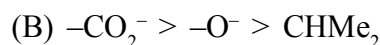
# ELECTRONIC DISPLACEMENT EFFECTS

## EXERCISE # I

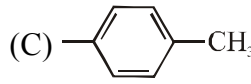
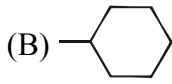
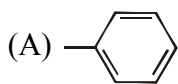
1. Which of the following is false order of -I effect ?



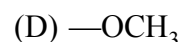
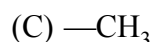
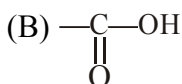
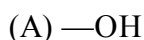
2. What is the correct order of inductive effect ?



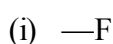
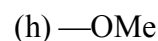
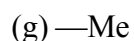
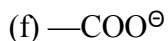
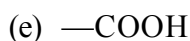
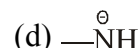
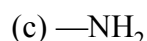
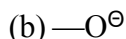
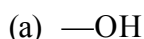
3. Which of the following groups have +I effect :



4. Which of the following groups have -I effect :



5. How many of the following groups have +I effect :



6. Which of the following statements is (are) true about resonance.

(a) Resonance is an intramolecular phenomenon.

(b) Resonance involves delocalization of both  $\sigma$  and  $\pi$  electrons.

(c) Resonance involves delocalization of  $\pi$  electrons only.

(d) Resonance decreases potential energy of an acyclic molecule.

(e) Resonance has no effect on the potential energy of a molecule.

(f) Resonance is the only way to increase molecular stability.

(g) Resonance is not the only way to increase molecular stability.

(h) Any resonating molecule is always more stable than any non resonating molecule.

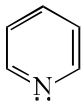
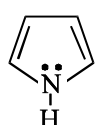
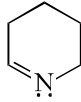
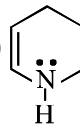
(i) The canonical structure explains all features of a molecule.

(j) The resonance hybrid explains all features of a molecule.

(k) Resonating structures are real and resonance hybrid is imaginary.

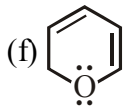
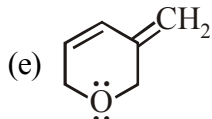
(l) Resonance hybrid is real and resonating structures are imaginary.

(m) Resonance hybrid is always more stable than all canonical structures.

7. Which of the following statement is incorrect ?  
 (A) Resonating structure are real & have real existence  
 (B) Equivalent contributing structures make resonance hybrid very stable.  
 (C) Contributing structures are hypothetical having no real existence  
 (D) Contributing structures are less stable than the resonance hybrid.
8. Which of the following is most stable.  
 (A) Conjugated alkadiene ( $\text{CH}_2 = \text{CH}-\text{CH} = \text{CH}_2$ )  
 (B) Isolated alkadiene ( $\text{CH}_2 = \text{CH}-\text{CH}_2-\text{CH} = \text{CH}_2$ )  
 (C) Cumulated alkadiene ( $\text{CH}_2 = \text{C} = \text{CH}_2$ )  
 (D) All are equally stable
9. Arrange the following resonating structure according to their contribution towards resonance hybrid?  
 (a)  $\text{CH}_2 = \overset{\oplus}{\text{N}} = \overset{\ominus}{\text{N}}$       (b)  $\overset{\ominus}{\text{CH}_2} - \text{N} = \overset{\oplus}{\text{N}}$       (c)  $\overset{\oplus}{\text{CH}_2} - \overset{\ominus}{\text{N}} = \overset{\ominus}{\text{N}}$       (d)  $\overset{\ominus}{\text{CH}_2} - \overset{\oplus}{\text{N}} \equiv \overset{\cdot\cdot}{\text{N}}$   
 (A)  $a > d > c > b$       (B)  $b > a > c > d$       (C)  $a > c > b > d$       (D)  $d > a > b > c$
10. A canonical structure will be more stable if  
 (A) it involves cyclic delocalization of  $(4n + 2) \pi$  - electrons than if it involves acyclic delocalization of  $(4n + 2) \pi$  - electrons.  
 (B) it involves cyclic delocalization  $(4n) \pi$  - electrons than if it involves acyclic delocalization of  $(4n) \pi$  - electrons.  
 (C) +ve charge is on more electronegative atom than if +ve charge is on less electronegative atom provided atoms are in the same period.  
 (D) -ve charge is on more electronegative atom than if -ve charge is on less electronegative atom provided atoms are in the same period.
11. Which one of the following pair of structures does not represent the phenomenon of resonance?  
 (A)  $\text{H}_2\text{C} = \text{CH} - \overset{\text{O}}{\parallel} \text{C} - \text{H}$  ;  $\overset{+}{\text{CH}_2} - \text{CH} = \overset{\text{O}^-}{\text{C}} - \text{H}$       (B)  $\text{CH}_2 = \text{CH} - \overset{+}{\text{CH}}\text{Cl}$  ;  $\overset{+}{\text{CH}_2} - \text{CH} = \text{CH} - \text{Cl}$   
 (C)  $(\text{CH}_3)_2\text{CH} - \overset{\text{O}}{\parallel} \text{C} - \text{O}^-$  ;  $(\text{CH}_3)_2\text{CH} - \overset{\text{O}^-}{\text{C}} = \text{O}$       (D)  $\text{CH}_3 - \text{CH}_2 - \overset{\text{O}}{\parallel} \text{C} - \text{CH}_3$  ;  $\text{CH}_3 - \text{CH} = \overset{\text{O}^-}{\text{C}} - \text{CH}_3$
12. In which of the following, lone-pair indicated is involved in resonance :  
 (a)       (b)       (c)       (d)   
 (e)  $\text{CH}_2 = \text{CH} - \text{CH}_2^{\oplus}$       (f)  $\text{CH}_2 = \text{CH} - \text{CH} = \overset{\cdot\cdot}{\text{N}}\text{H}$

13. In which of the following lone-pair indicated is not involved in resonance :

- (a)  $\text{CH}_2 = \text{CH} - \ddot{\text{N}}\text{H} - \text{CH}_3$  (b)  $\text{CH}_2 = \text{CH} - \text{CH} = \ddot{\text{O}}:$   
 (c)  $\text{CH}_2 = \text{CH} - \ddot{\text{O}}: - \text{CH} = \text{CH}_2$  (d)  $\text{CH}_2 = \text{CH} - \text{C} \equiv \text{N}:$



14. Which of the following groups cannot participate in resonance with other suitable group :

- (a)  $-\text{COOH}$  (b)  $-\text{COOCH}_3$  (c)  $-\text{COCl}$  (d)  $-\text{NH}_3^+$   
 (e)  $-\text{CH}_2^+$

15. Identify electron donating groups in resonance among the following :

- (a)  $-\text{CONH}_2$  (b)  $-\text{NO}_2$  (c)  $-\text{OCOCH}_3$  (d)  $-\text{COOCH}_3$   
 (e)  $-\text{CHO}$  (f)  $-\text{NHCOCH}_3$

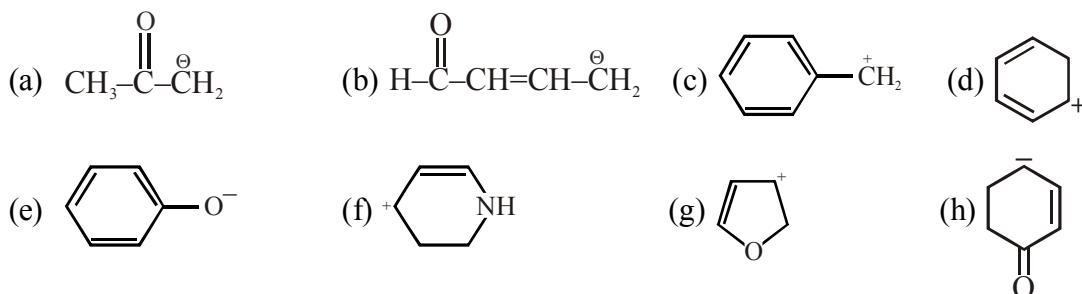
16. Identify electron withdrawing groups in resonance among the following :

- (a)  $-\text{COOH}$  (b)  $-\text{CONHCH}_3$  (c)  $-\text{COCl}$  (d)  $-\text{CN}$   
 (e)  $-\text{O} - \text{CH} = \text{CH}_2$  (f)

17. Which of the following groups can either donate or withdraw a pair of electrons in resonance depending upon situation :

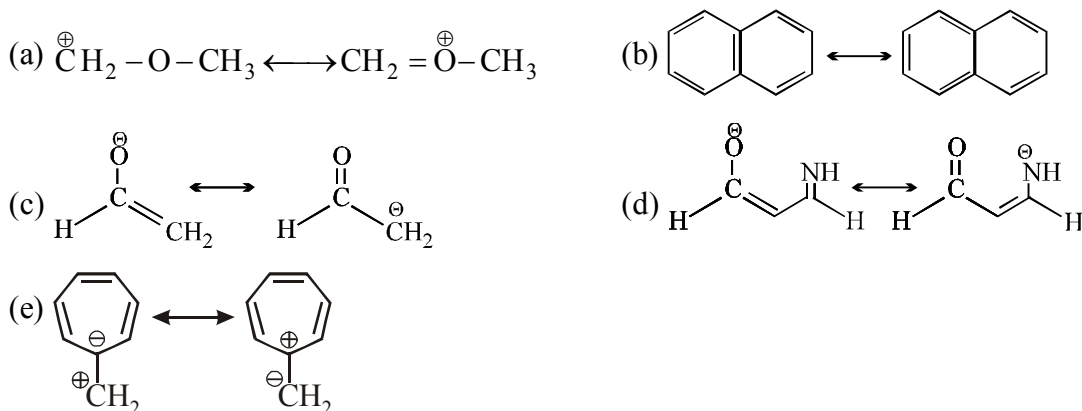
- (a)  $-\text{NO}_2$  (b)  $-\text{NO}$  (c)  $-\text{CH} = \text{CH}_2$  (d)  $-\text{CHO}$   
 (e)  $-\text{NH}_2$  (f)  $-\text{N} = \text{NH}$

18. Draw the resonance forms to show the delocalization of charges in the following ions

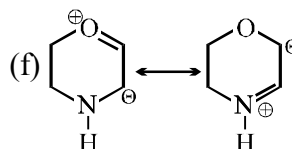
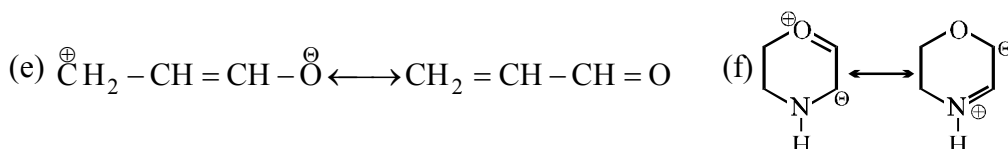
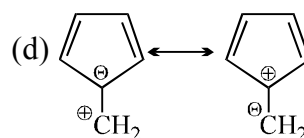
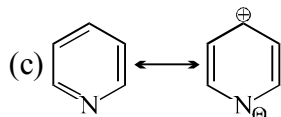
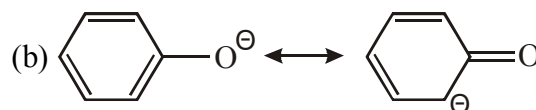
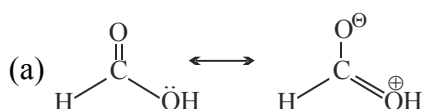


- (i)  $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH} = \text{CH} - \text{CH}^+ - \text{CH}_3$  (j)  $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH} = \text{CH} - \text{CH}_2^+$

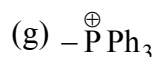
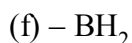
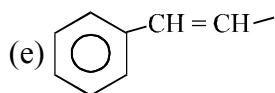
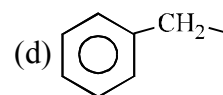
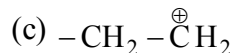
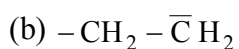
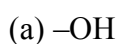
19. Identify less stable canonical structure in each of the following pairs :



20. Identify more stable canonical structure in each of the following pairs :



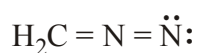
21. Which of the following group can participate in resonance with other suitable group :



22. Consider structural formulas A, B and C:



(A)



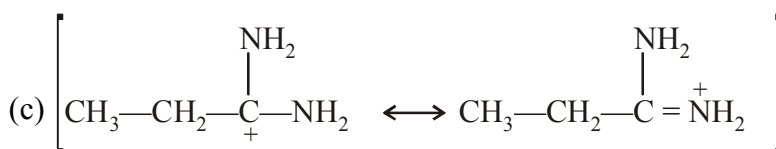
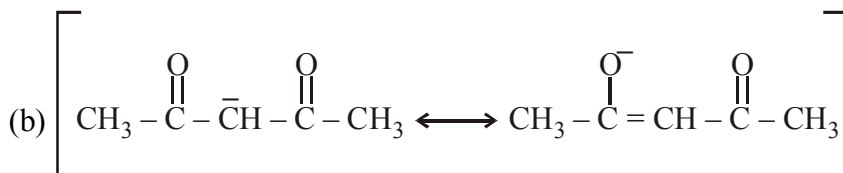
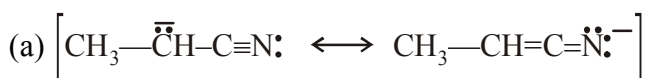
(B)



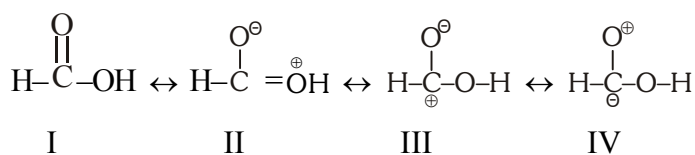
(C)

- Are A, B and C isomers, or are they resonance forms ?
- Which structures have a negatively charged carbon?
- Which structures have a positively charged carbon?
- Which structures have a positively charged nitrogen?
- Which structures have a negatively charged nitrogen?
- What is the net charge on each structure?
- Which is a more stable structure, A or B? Why?
- Which is a more stable structure, B or C? Why?

23. In each of the following pairs of resonating structure which resonating structure is more stable :



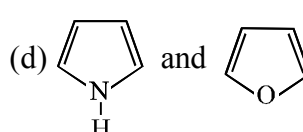
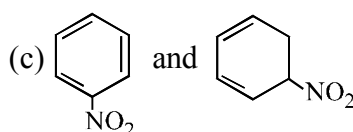
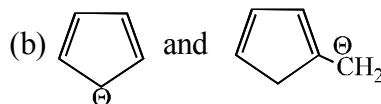
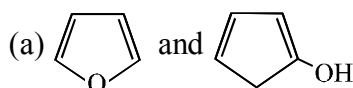
24. Formic acid is considered as a hybrid of the four structures



Which of the following order is correct for the stability of four contributing structures.

(A) I > II > III > IV (B) I > II > IV > III (C) I > III > II > IV (D) I > IV > III > II

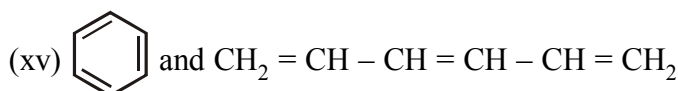
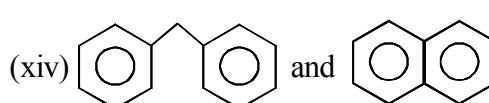
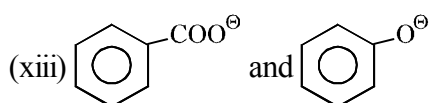
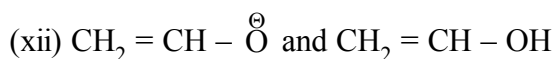
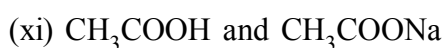
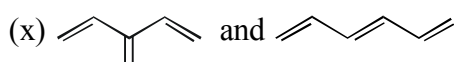
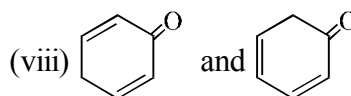
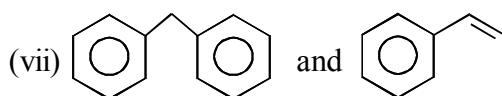
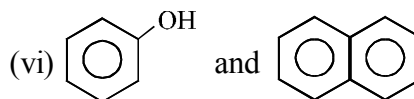
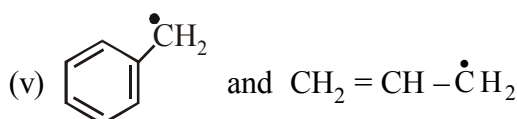
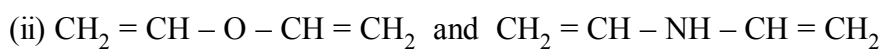
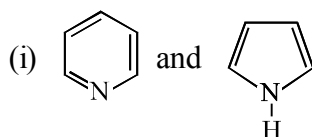
25. In the given pair of compounds select the one in each pair having lesser resonance energy :



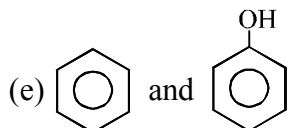
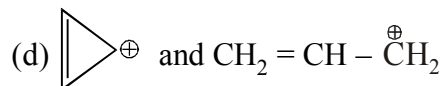
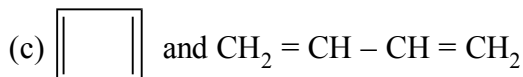
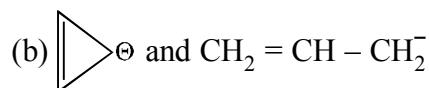
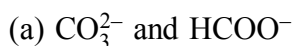
26. Resonance energy of resonance hybrid of a molecule will be more if :

- (a) canonical structures are equivalent than if canonical structures are non-equivalent  
(b) molecule is aromatic than if molecule is not aromatic.

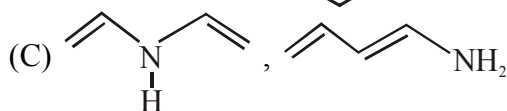
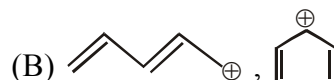
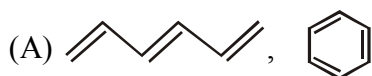
27. In the given pair of compounds select the one in each pair having higher resonance energy :



28. In the given pair of compounds select the one in each pair having lesser resonance energy :

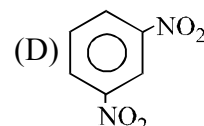
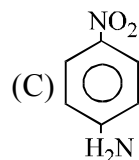
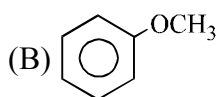
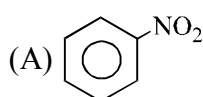


29. In which of the following pairs first one is having more resonance energy than the second one -

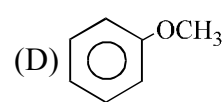
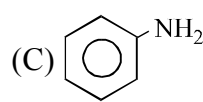
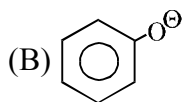
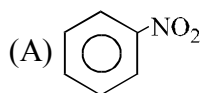


(D) None of these

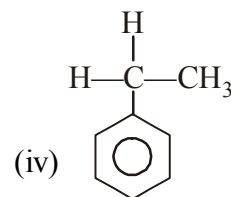
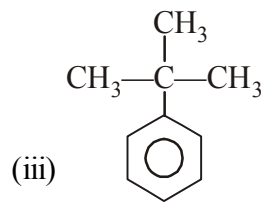
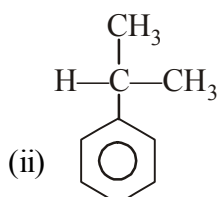
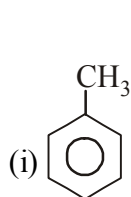
30. In which of the following molecules  $\pi$  - electron density in ring is minimum :



31. In which of the following molecules  $\pi$  - electron density in ring is maximum :



32. Arrange following compounds in decreasing order of reactivity of ring towards attack of electron deficient species -



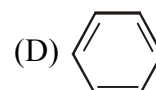
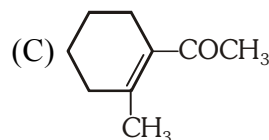
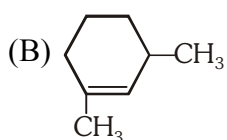
(A)  $i > ii > iii > iv$

(B)  $iii > iv > ii > i$

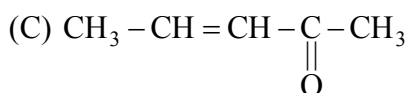
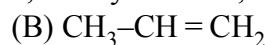
(C)  $i > iv > ii > iii$

(D)  $i > ii > iv > iii$

33. In which of the following molecule all the effect namely inductive, mesomeric & hyperconjugation operate:



34. Which one of the following molecules has all the effect, namely inductive, mesomeric and hyperconjugative?


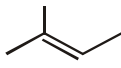
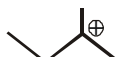


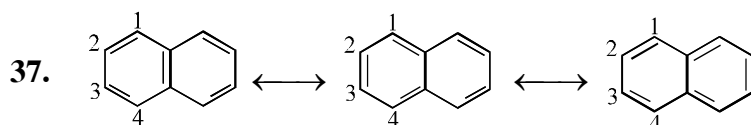
35. Select the correct statement.

- (i) Delocalisation of  $\sigma$ -electron is hyperconjugation.  
 (ii) Delocalisation of  $\pi$ -electron is resonance.  
 (iii) Permanent partial displacement of  $\sigma$ -electron is inductive effect.

(A) i & iii (B) ii & iii (C) i & ii (D) i, ii, iii

36. Which of the following compound is correctly matched with number of hyperconjugating structures (involving C—H bond) :

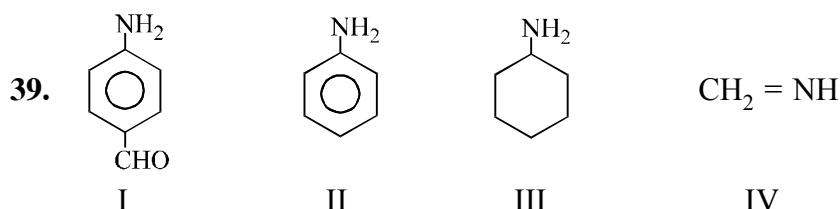
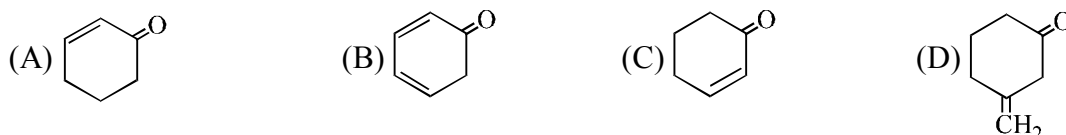
- (A)  (3) (B)  (9) (C)  (8) (D)  $\text{CH}_3\text{—C}\equiv\text{C—CH}_3$  (5)



These are three canonical structures of naphthalene. Examine them and find correct statement among the following :

- (A) All C—C bonds are of same length (B) C1—C2 bond is shorter than C2—C3 bond.  
 (C) C1—C2 bond is longer than C2—C3 bond (D) None

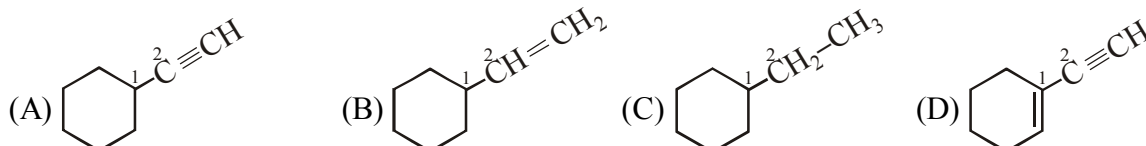
38. Which of the following has longest C—O bond :



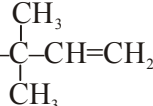
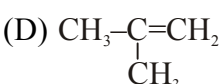
Among these compounds, the correct order of C—N bond lengths is :

- (A) IV > I > II > III (B) III > I > II > IV (C) III > II > I > IV (D) III > I > IV > II

40. C1—C2 bond is shortest in



41. Which of the following molecule has longest C=C bond length ?

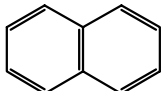
- (A)  $\text{CH}_2=\text{C}=\text{CH}_2$  (B)  $\text{CH}_3\text{—CH=CH}_2$  (C)  (D) 



42. Which of the following molecule has shortest C=C bond length ?

- (A)  $\text{CH}_2=\text{C}=\text{CH}_2$  (B)  $\text{CH}_3-\text{CH}=\text{CH}_2$  (C)  $\text{CH}_3-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}=\text{CH}_2$  (D)  $\text{CH}_3-\overset{\text{CH}_3}{\text{C}}=\text{CH}_2$

43. C—C and C=C bond lengths are unequal in :

- (A) Benzene (B) 1,3-butadiene (C) 1,3-cyclohexadiene (D) 

44. Among the following molecules, the correct order of C—C bond length is ( $\text{C}_6\text{H}_6$  is benzene)

- (A)  $\text{C}_2\text{H}_6 > \text{C}_2\text{H}_4 > \text{C}_6\text{H}_6 > \text{C}_2\text{H}_2$  (B)  $\text{C}_2\text{H}_6 > \text{C}_6\text{H}_6 > \text{C}_2\text{H}_4 > \text{C}_2\text{H}_2$   
 (C)  $\text{C}_2\text{H}_4 > \text{C}_2\text{H}_6 > \text{C}_2\text{H}_2 > \text{C}_6\text{H}_6$  (D)  $\text{C}_2\text{H}_6 > \text{C}_2\text{H}_4 > \text{C}_2\text{H}_2 > \text{C}_6\text{H}_6$

45.  $\text{CH}_3\text{O}-\text{CH}=\text{CH}-\text{NO}_2$  I

$\text{CH}_2=\text{CH}-\text{NO}_2$  II

$\text{CH}_2=\text{CH}-\text{Cl}$  III

$\text{CH}_2=\text{CH}_2$  IV

Which of the following is the correct order of C—C bond lengths among these compounds :

- (A)  $\text{I} > \text{II} > \text{III} > \text{IV}$  (B)  $\text{IV} > \text{III} > \text{II} > \text{I}$  (C)  $\text{I} > \text{III} > \text{II} > \text{IV}$  (D)  $\text{II} > \text{III} > \text{I} > \text{IV}$

46. Which of the following is (are) the correct order of bond lengths :

- (A)  $\text{C}-\text{C} > \text{C}=\text{C} > \text{C}\equiv\text{C} > \text{C}\equiv\text{N}$  (B)  $\text{C}=\text{N} > \text{C}=\text{O} > \text{C}=\text{C}$   
 (C)  $\text{C}=\text{C} > \text{C}=\text{N} > \text{C}=\text{O}$  (D)  $\text{C}-\text{C} > \text{C}=\text{C} > \text{C}\equiv\text{C} > \text{C}-\text{H}$

47. In which of the following pairs, indicated bond having less bond dissociation energy :

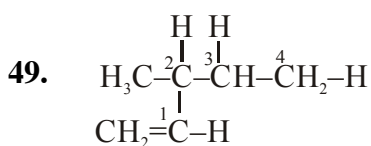
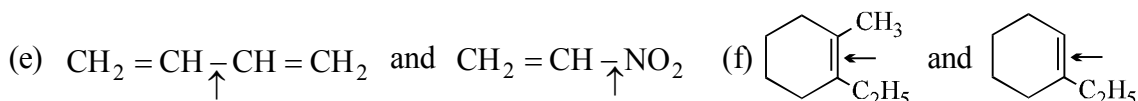
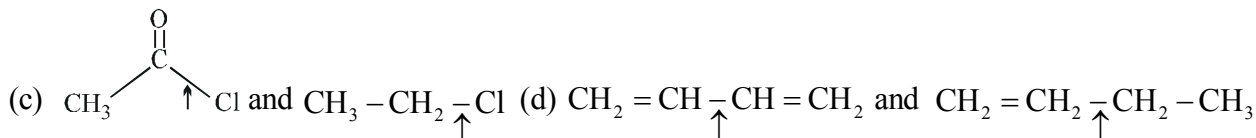
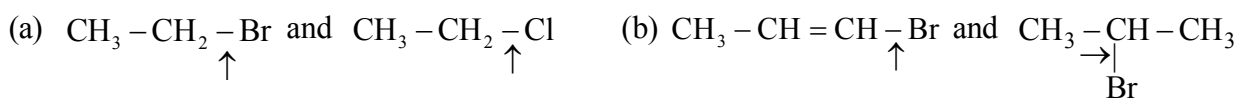
- (a)  and  $\text{CH}_2=\text{CH}_2$  (b)  $\text{CH}_3-\text{C}\equiv\text{CH}$  and  $\text{HC}\equiv\text{CH}$   
 (Arrows point to the C≡C bond in both molecules)

- (c)  $\text{CH}_2=\text{CH}-\text{C}(\text{CH}_2)=\text{CH}_2$  and  $\text{CH}_2=\text{CH}-\text{C}(\text{CH}_2)=\text{CH}_2$   
 (Arrows point to the C—C single bond in both molecules)

- (d)  $\text{H}_2\text{N}-\text{C}(=\text{O})-\text{NH}_2$  and  $\text{CH}_3-\text{C}(=\text{O})-\text{NH}_2$  (e)  $\text{Cl}-\text{C}(=\text{O})-\text{Cl}$  and  $\text{CH}_3-\text{C}(=\text{O})-\text{Cl}$   
 (Arrows point to the C—O bond in both molecules)

- (f)  $\text{H}_2\text{N}-\text{C}(=\text{O})-\text{NH}_2$  and  $\text{H}-\text{C}(=\text{O})-\text{NH}_2$   
 (Arrows point to the C—O bond in both molecules)

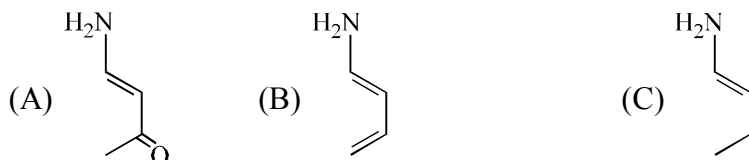
48. In which of the following pairs, indicated bond is of greater strength :



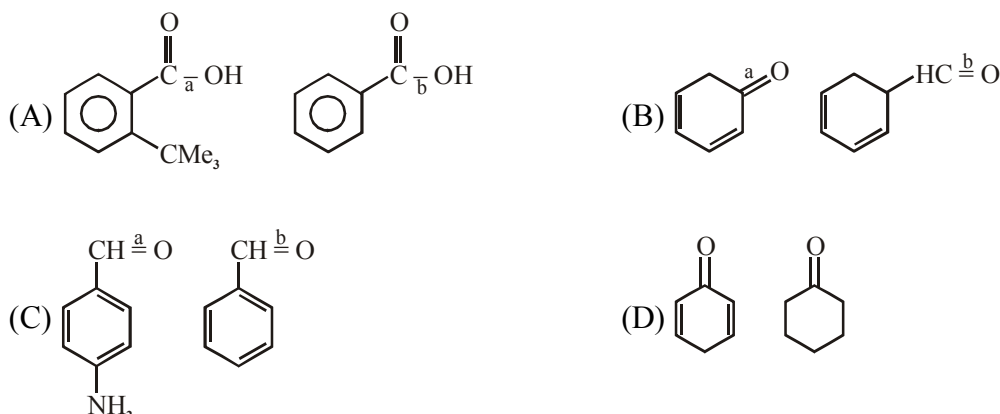
the correct order of bond dissociation energy (provided bond undergoes homolytic cleavage):

- (A)  $\text{C}^2-\text{H} > \text{C}^3-\text{H} > \text{C}^4-\text{H} > \text{C}^1-\text{H}$  (B)  $\text{C}^2-\text{H} > \text{C}^3-\text{H} > \text{C}^1-\text{H} > \text{C}^4-\text{H}$   
(C)  $\text{C}^1-\text{H} > \text{C}^4-\text{H} > \text{C}^2-\text{H} > \text{C}^3-\text{H}$  (D)  $\text{C}^1-\text{H} > \text{C}^4-\text{H} > \text{C}^3-\text{H} > \text{C}^2-\text{H}$

50. Compare the C-N bond-length in the following species:

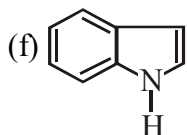
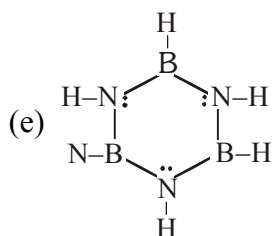
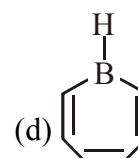
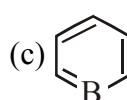
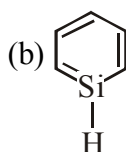
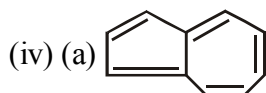
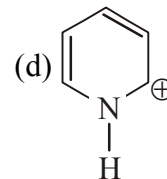
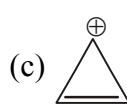
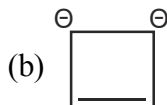
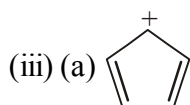
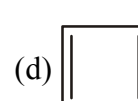
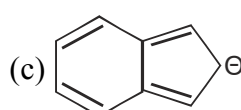
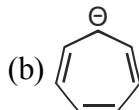
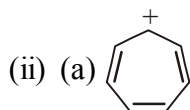
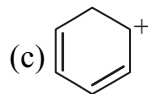
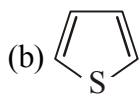
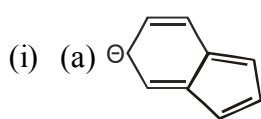


51. In which case, C - O bond length is shorter for I<sup>st</sup> compound :

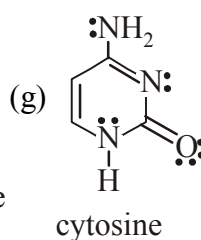
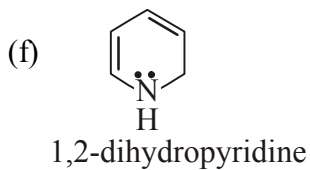
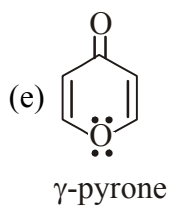
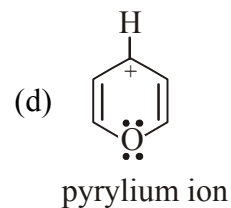
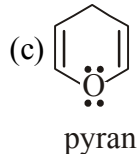
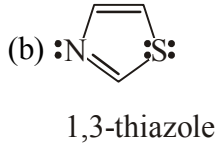
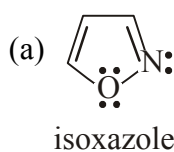


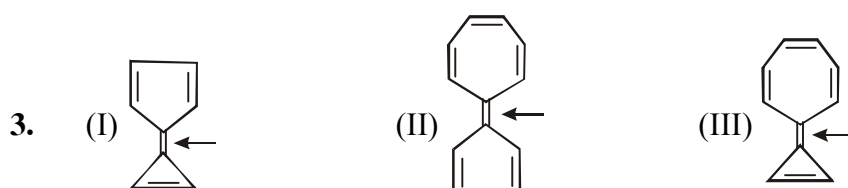
## EXERCISE # II

1. In each set of species select the aromatic species.



2. Which of the given compound is aromatic, antiaromatic or nonaromatic.

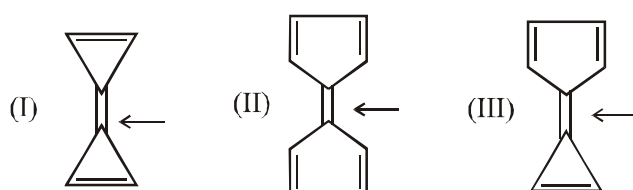




Compare carbon-carbon bond rotation across I, II, III.

- (A)  $I > II > III$  (B)  $I > III > II$  (C)  $II > I > III$  (D)  $II > III > I$

4. Which of the given compounds has minimum rotation energy barrier across indicated carbon-carbon bond.

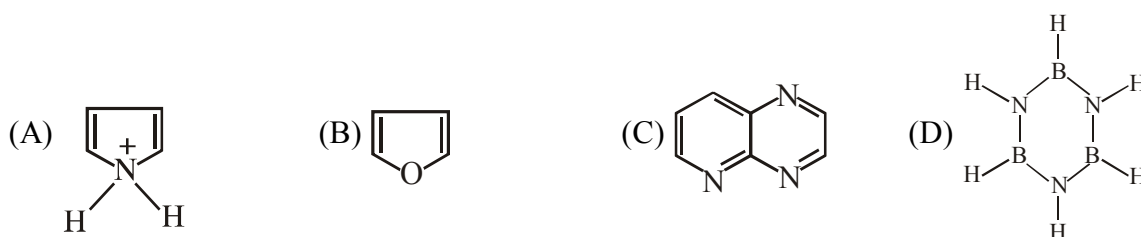


- (A) I (B) II (C) III (D) All are equal

5. Which species is not aromatic ?



6. Which of the following are non-aromatic



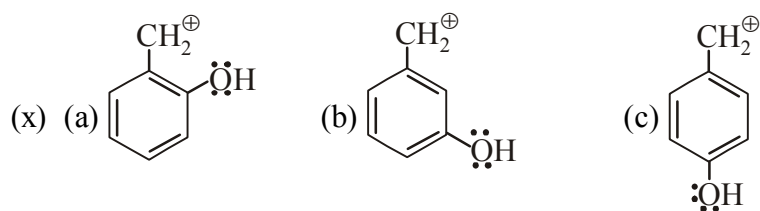
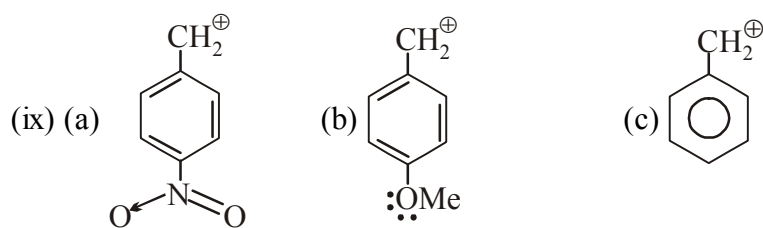
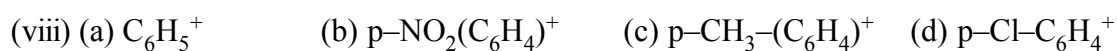
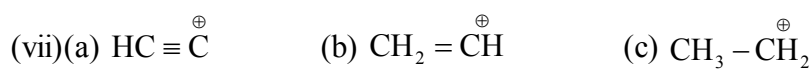
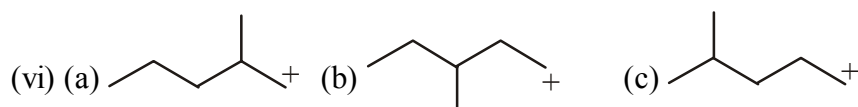
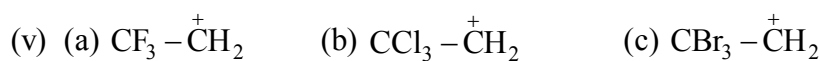
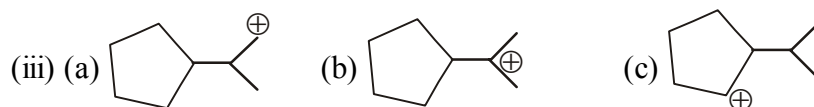
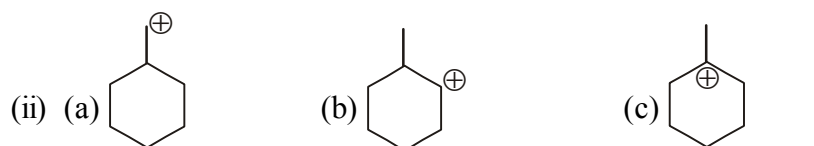
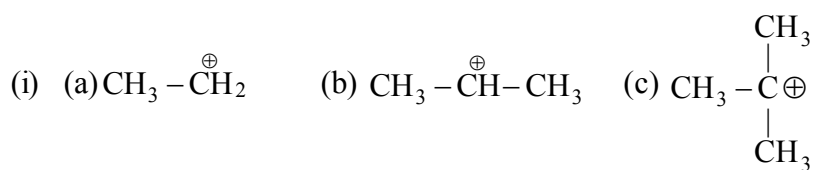
7. Write down the structure of the following molecule and comment on aromaticity ?

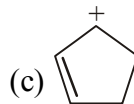
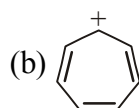
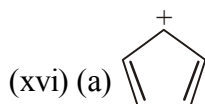
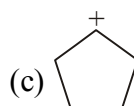
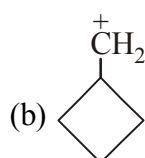
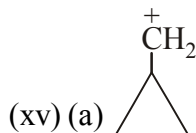
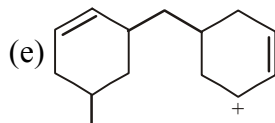
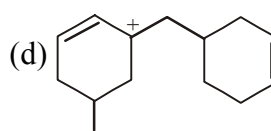
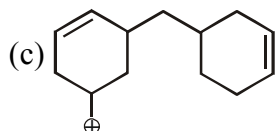
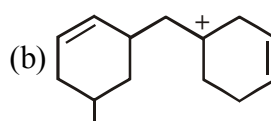
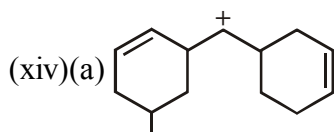
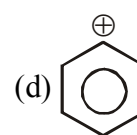
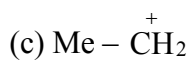
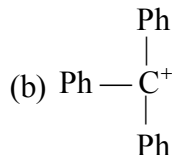
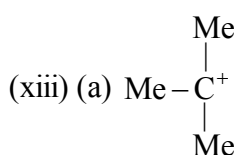
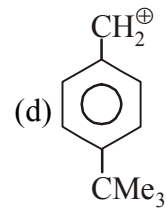
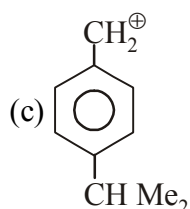
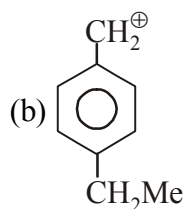
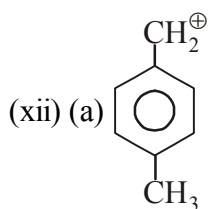
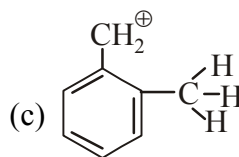
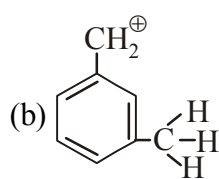
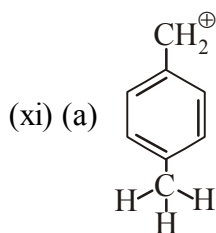
- (a)  $B_3H_3O_3$  (b)  $C_3N_3(NH_2)_3$  (c) Trimer of isocyanic acid ( $HN=C=O$ )<sub>3</sub>

8. Select the least stable one :

- (A)  $CH_3-CH_2^+$  (B)  $CH_3-CH_2-CH_2^+$   
 (C)  $H_3C > CH-CH_2^+$  (D)  $H_3C > C-CH_2^+$

9. Write stability in decreasing order of following intermediates:





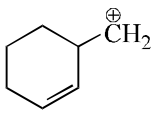
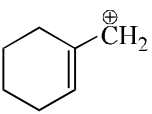
10. Consider the following statements:

- (I)  $\text{CH}_3\text{O}^+\text{CH}_2$  is more stable than  $\text{CH}_3\text{CH}_2^+$  (II)  $\text{Me}_2\text{CH}^+$  is more stable than  $\text{CH}_3\text{CH}_2\text{CH}_2^+$   
 (III)  $\text{CH}_2=\text{CH}-\text{CH}_2^+$  is more stable than  $\text{CH}_3\text{CH}_2\text{CH}_2^+$  (IV)  $\text{CH}_2=\text{CH}^+$  is more stable than  $\text{CH}_3\text{CH}_2^+$

Of these statements:

- (A) I and II are correct (B) III and IV are correct  
 (C) I, II and III are correct (D) II, III and IV are correct

11. In each of the following pairs of ions which ion is more stable:

- (a) (I)  $\text{C}_6\text{H}_5-\text{CH}_2^+$  and (II)  $\text{CH}_2=\text{CH}-\text{CH}_2^+$  (b) (I)  $\text{CH}_3-\text{CH}_2^+$  and (II)  $\text{CH}_2=\text{CH}^+$   
 (c) (I)  and (II)  (d) (I)  $\text{CH}_3-\text{CH}(\text{CH}_3)-\text{CH}_3$  and (II)  $\text{CH}_3-\text{N}(\text{CH}_3)-\text{CH}_3$   
 $\text{CH}_3-\text{C}^+(\text{CH}_3)-\text{CH}_3$   $\text{CH}_3-\text{C}^+(\text{CH}_3)-\text{CH}_3$

12. Find out correct stability order in the following carbocations-

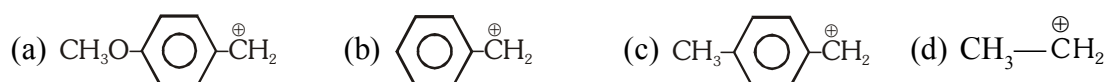


- (A) IV > I > III > II (B) IV > III > I > II (C) I > IV > III > II (D) I > III > IV > II

13. Which of the following carbonium ion is most stable ?

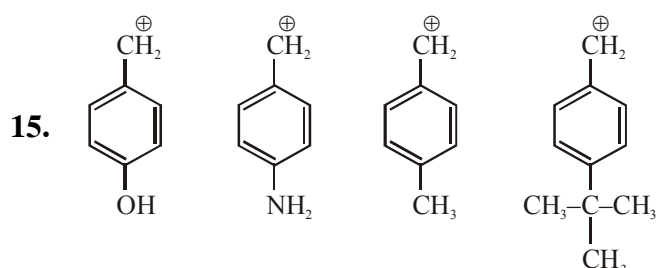
- (A)  $\text{Ph}_3\text{C}^+$  (B)  $(\text{CH}_3)_3\text{C}^+$  (C)  $(\text{CH}_3)_2\text{CH}^+$  (D)  $\text{CH}_2=\text{CH}-\text{CH}_2^+$

14. Consider the following carbocations



The relative stabilities of these carbocations are such that :-

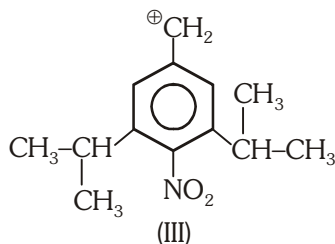
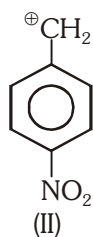
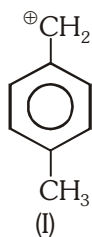
- (A) d < b < c < a (B) b < d < c < a  
 (C) d < b < a < c (D) b < d < a < c



Correct order of carbocation stability is :

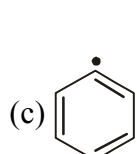
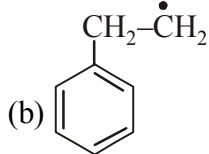
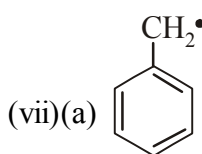
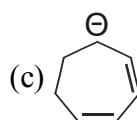
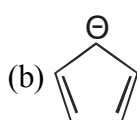
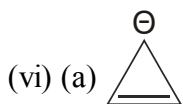
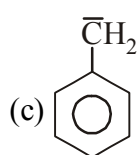
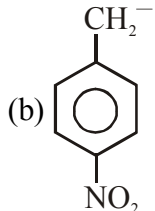
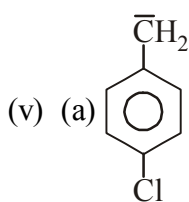
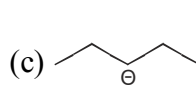
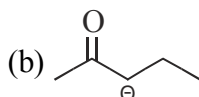
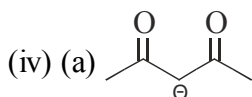
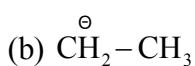
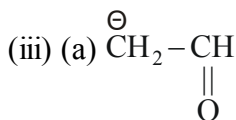
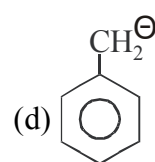
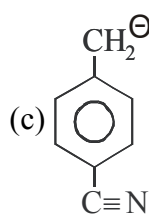
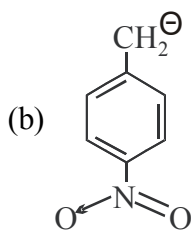
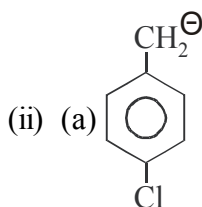
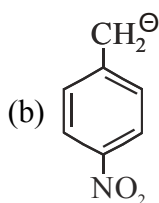
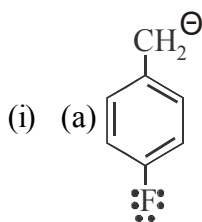
- (A) 2 > 1 > 4 > 3 (B) 1 > 2 > 4 > 3 (C) 3 > 4 > 2 > 1 (D) 2 > 1 > 3 > 4

16. Arrange the following carbocation in the increasing order of stability :

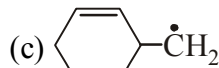
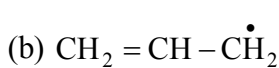
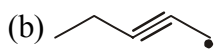
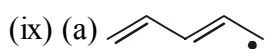
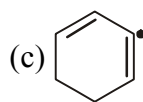
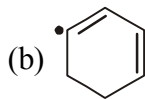
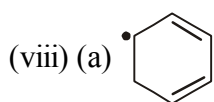


- (A) I < II < III      (B) II < III < I      (C) III < II < I      (D) III < I < II

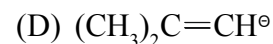
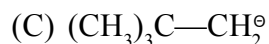
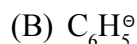
17. Rank the following sets of intermediates in increasing order of their stability.



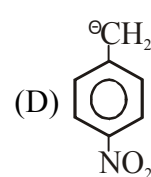
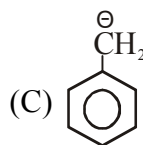
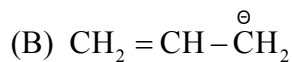
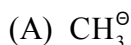




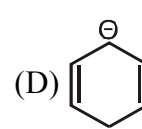
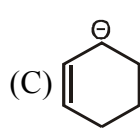
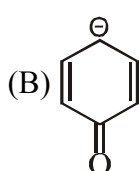
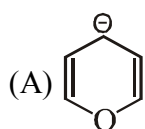
18. Most stable carbanion is :-



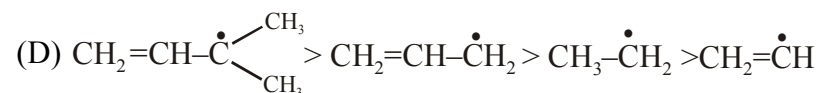
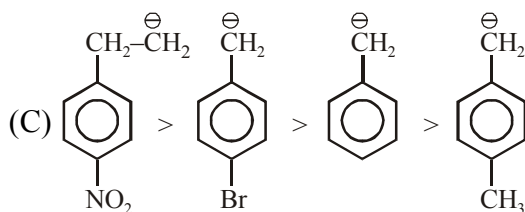
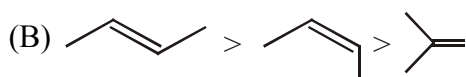
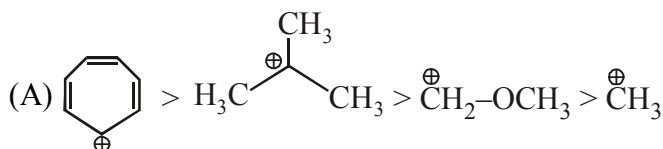
19. Most stable carbanion is :



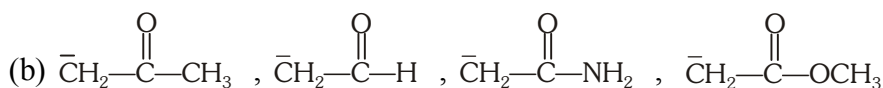
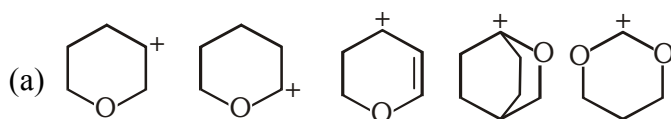
20. Identify the most stable anion.



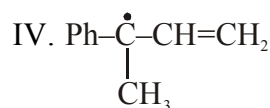
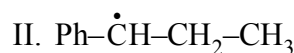
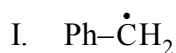
21. Correct order of stability :



22. Rank the following sets of intermediates in increasing order of their stability giving appropriate reasons for your choice.



23. Select the correct order of stability of carbon free radicals :



(A)  $\text{IV} > \text{III} > \text{I} > \text{II}$  (B)  $\text{IV} > \text{III} > \text{II} > \text{I}$  (C)  $\text{I} > \text{II} > \text{III} > \text{IV}$  (D)  $\text{I} > \text{III} > \text{II} > \text{IV}$

24.  $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH} - \text{CH}_3$  is more stable than  $\text{CH}_3 - \text{CH} = \text{C} = \text{CH} - \text{CH}_3$  because

(I)

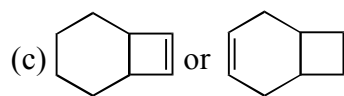
(II)

(A) there is resonance in I but not in II (B) there is tautomerism in I but not in II  
(C) there is hyperconjugation in I but not in II (D) II has more cononical structures than I.

25. Choose the more stable alkene in each of the following pairs. Explain your reasoning.

(a) 1-Methylcyclohexene or 3-methylcyclohexene

(b) Isopropenylcyclopentane or allylcyclopentane



26. Match each alkene with the appropriate heat of combustion:

Heats of combustion (kJ/mol) : 5293 ; 4658; 4650; 4638; 4632

(a) 1-Heptene

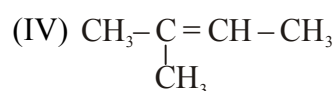
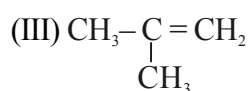
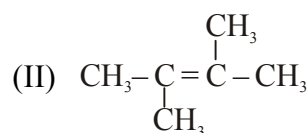
(b) 2,4-Dimethyl-1-pentene

(c) 2,4-Dimethyl-2-pentene

(d) 4,4-Dimethyl-2-pentene

(e) 2,4,4-Trimethyl-2-pentene

27. Stability of :



in the increasing order is :

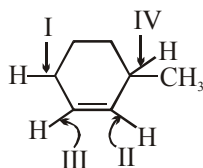
(A)  $\text{I} < \text{III} < \text{IV} < \text{II}$

(B)  $\text{I} < \text{II} < \text{III} < \text{IV}$

(C)  $\text{I} < \text{IV} < \text{III} < \text{I}$

(D)  $\text{II} < \text{III} < \text{IV} < \text{I}$

28. Which of the following C-H bonds participate in hyperconjugation ?



- (A) I and II      (B) I and IV      (C) I and III      (D) III and IV

29. Rank the following alkenes in decreasing order of heat of combustion values :



(I)



(II)



(III)



(IV)

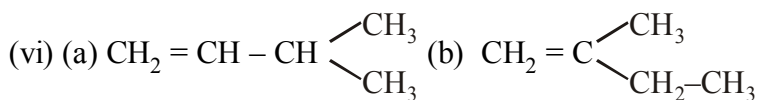
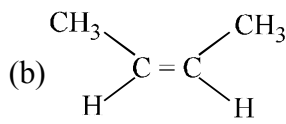
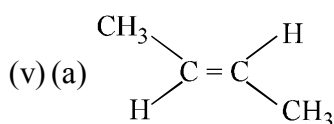
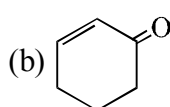
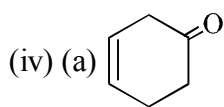
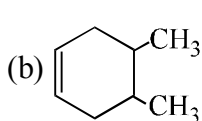
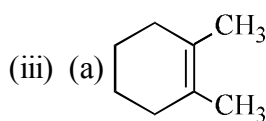
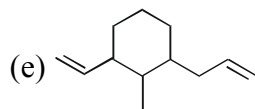
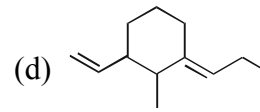
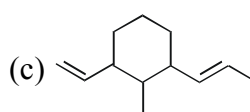
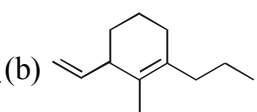
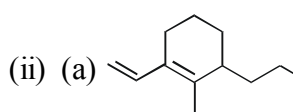
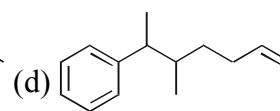
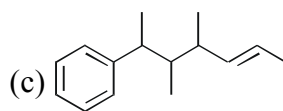
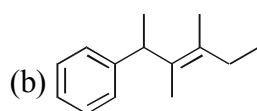
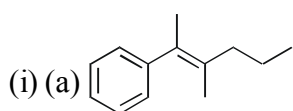
(A) II > III > IV > I

(B) II > IV > III > I

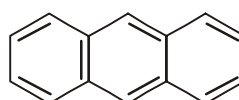
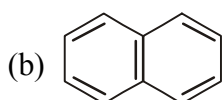
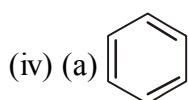
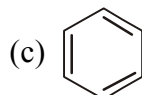
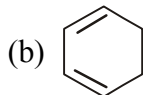
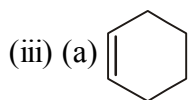
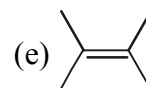
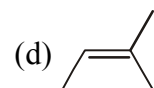
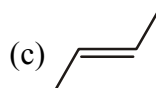
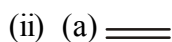
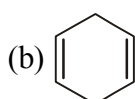
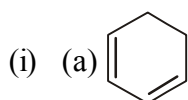
(C) I > III > IV > II

(D) I > IV > III > II

30. Write decreasing order of heat of hydrogenation :

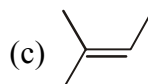
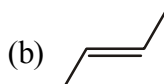
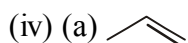
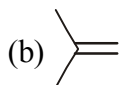
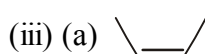
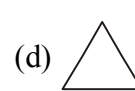
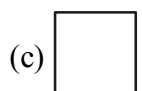
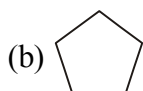
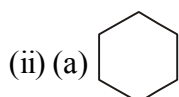
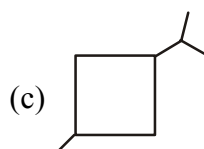
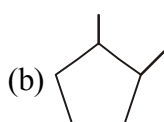
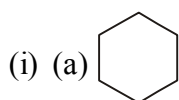


31. Write increasing order of heat of hydrogenation :

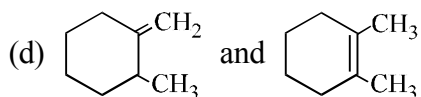
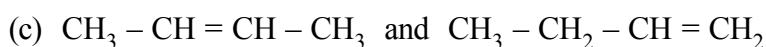
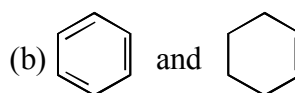
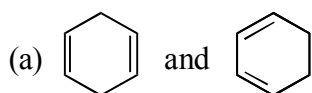


(HOH per benzene ring)

32. Give decreasing order of heat of combustion (HOC):



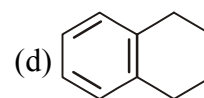
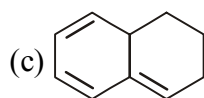
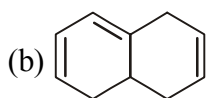
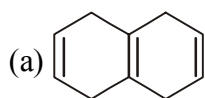
33. Among the following pairs identify the one which gives higher heat of hydrogenation :



34. Arrange the following compounds in order of :

(I) Stability

(II) Heat of hydrogenation



35. If Heat of hydrogenation of 1-butene is 30 Kcal/mol then heat of hydrogenation of 1,3-butadiene is ?

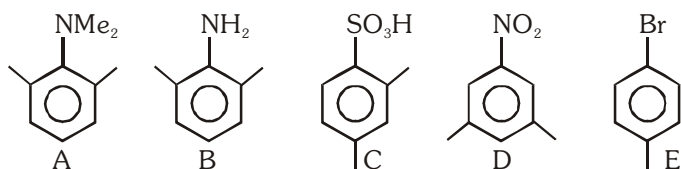
(A) 30

(B) 60

(C) 57

(D) 25

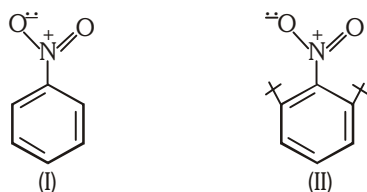
36.



Steric inhibition of resonance takes place :

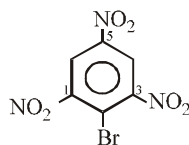
- (A) In A,B only      (B) In A, B, C, E      (C) C only      (D) In A only

37. Consider the following two structures and choose the correct statements -



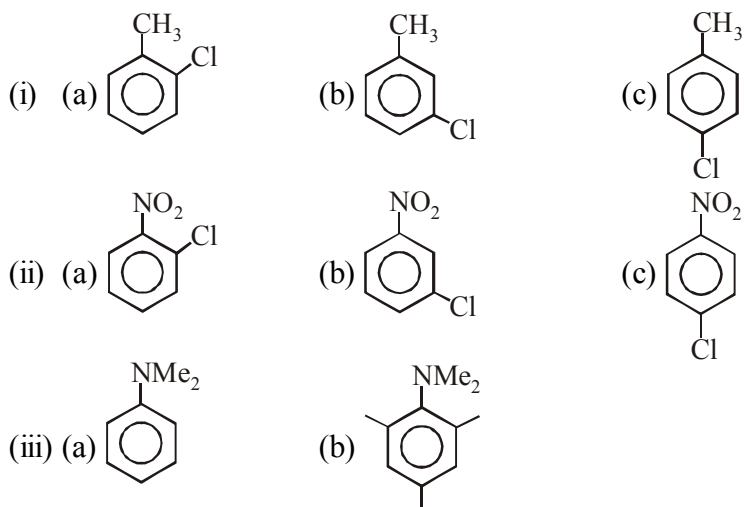
- (A) carbon-nitrogen bond length structure I is greater than that in structure II  
 (B) carbon-nitrogen bond length in structure I is less than in structure II  
 (C) carbon-nitrogen bond length in both structure is same  
 (D) It can not be compared

38. Which of the following statements would be true about this compound :



- (A) All three C – N bonds are of same length.  
 (B) C1 – N and C3 – N bonds are of same length but shorter than C5 – N bond.  
 (C) C1 – N and C3 – N bonds are of same length but longer than C5 – N bond.  
 (D) C1 – N and C3 – N bonds are of different length but both are longer than C5 – N bond

39. Arrange given compounds in decreasing order of dipole moment :

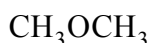
40. Why a cation like  is not possible.

EXERCISE # III

1. Cyclopentadienyl anion is much more stable than allyl anion because :

- (A) Cyclic anion is more stable than acyclic anion
- (B) Delocalised anion is more stable than localised anion
- (C) Cyclopentadienyl anion is aromatic in nature
- (D) None of these

2. Select correct statement regarding given compounds :



I

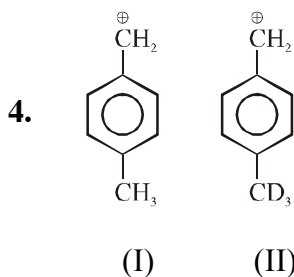


II

- (A) Boiling point of II is higher than I
- (B) Boiling point of II is lower than I
- (C) Compound I forms intramolecular H-bonding
- (D) Compound II forms intermolecular H-bonding

3. In the compound,  $\text{CH}_3\text{—CH=CH—C}\equiv\text{N}$ , the most electronegative carbon is :

- (A) I
- (B) II
- (C) III
- (D) IV



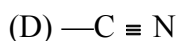
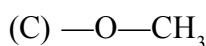
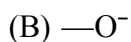
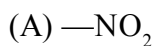
Carbocation (I) is more stable than carbocation (II), because :

- (A)  $\text{—CD}_3$  has more + I effect than  $\text{—CH}_3$
- (B)  $\text{—CH}_3$  has more + I effect than  $\text{—CD}_3$
- (C)  $\text{—CH}_3$  has more + H effect than  $\text{—CD}_3$
- (D)  $\text{—CD}_3$  has more + H effect than  $\text{—CH}_3$

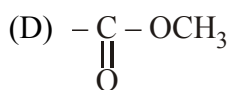
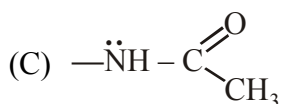
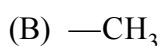
5. Select correct statement :

- (A) Carbon-oxygen bonds are of equal length in acetate ion
- (B) Resonating structures of acetate ion are equivalent
- (C) Carbon-oxygen bonds are of unequal length in formate ion
- (D) Resonating structures of formate ion are equivalent

6. Match the column I with column II.

**Column-I****(Group attached with benzene ring)****Column-II****(Effect shown by the group)**(P)  $\text{—R effect}$ (Q)  $\text{+R effect}$ (R)  $\text{+I effect}$ (S)  $\text{—I effect}$ 

7. **Column- I**

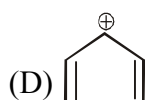
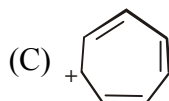
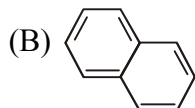
**(Groups attached to phenyl ring)****Column- II****(Effect shown)**(P)  $\text{+M}$ (Q)  $\text{—M}$ (R)  $\text{+H}$ (S)  $\text{—I}$ 

8. Match the column :

**Column-I**(A) Group donate  $\text{e}^-$  inductively but does not donate / withdraw by resonance(B) Group withdraw  $\text{e}^-$  inductively but does not donate / withdraw by resonance(C) Group withdraw  $\text{e}^-$  inductively & donate  $\text{e}^-$  by resonance(D) Group withdraw  $\text{e}^-$  inductively & withdraw  $\text{e}^-$  by resonance**Column-II**(P)  $\text{—OH}$ (Q)  $\text{—NO}_2$ (R)  $\text{—CH}_2\text{—CH}_3$ (S)  $\text{—}\overset{+}{\text{N}}\text{H}_3$ (T)  $\text{—NH}_2$

9. Match the column I with column II.

Column-I



Column-II

(P) Aromatic

(Q) Non-aromatic

(R) Anti-aromatic

(S) Cyclic structure

10. **Statement-I :** bond length  $a < b$

**Because**

**Statement-II :** More is the double bond character less is the bond length.

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

11. **Statement-I :**  $\text{Me}_3\text{C}^+$  is more stable than  $\text{Me}_2\text{CH}^+$  and  $\text{Me}_2\text{CH}^+$  is more stable than the  $\text{MeCH}_2^+$ .

**Because**

**Statement-II :** Greater the number of hyperconjugative structures, more is the stability of carbocation.

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

12. **Statement-I :** The potential energy barrier for rotation about  $\text{C}=\text{C}$  bond in 2-butene is much higher than that in ethylene.

**Because**

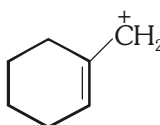
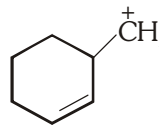
**Statement-II :** Hyperconjugation effect decreases the double bond character.

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

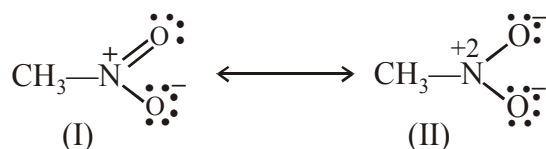




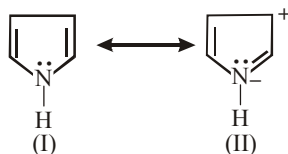
18. In which of the following cases, the carbocation (I) is less stable than the carbocation (II) ?

- (A)  $\text{C}_6\text{H}_5-\dot{\text{C}}\text{H}_2$  (I),  $\text{CH}_2=\text{CH}-\dot{\text{C}}\text{H}_2$  (II)      (B)  (I),  (II)
- (C)  $\text{CH}_2=\dot{\text{C}}\text{H}$  (I),  $\text{CH}_3-\dot{\text{C}}\text{H}_2$  (II)      (D)  $\text{H}_3\text{C}-\dot{\text{C}}\text{H}_2$  (I),  $\text{CH}_2-\overset{\oplus}{\underset{\text{F}}{\text{C}}}-\text{CH}_2$  (II)

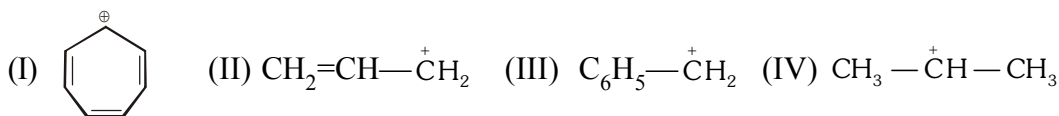
19. Examine the structures I and II for nitromethane and choose the statement correctly :



- (A) Structure II is unlikely representation because electrons have shifted to oxygen  
 (B) Structure II is unlikely representation because nitrogen has sextet of electrons  
 (C) Structure II is acceptable and important  
 (D) None of these
20. Examine the following two structures for pyrrole and choose the correct statement given below



- (A) II is not an acceptable resonating structure because carbonium ions is less stable than nitride ion  
 (B) II is not an acceptable resonating structure because there is charge separation  
 (C) II is not an acceptable resonating structure because nitrogen has ten valance electrons  
 (D) II is an acceptable resonating structure
21. Delocalization of electrons increases molecular stability because :
- (A) Potential energy of the molecule decreases    (B) Electron-electron repulsion decreases  
 (C) Both (A) and (B)    (D) Electron-electron repulsion increases
22. The most stable and the least stable carbocation among



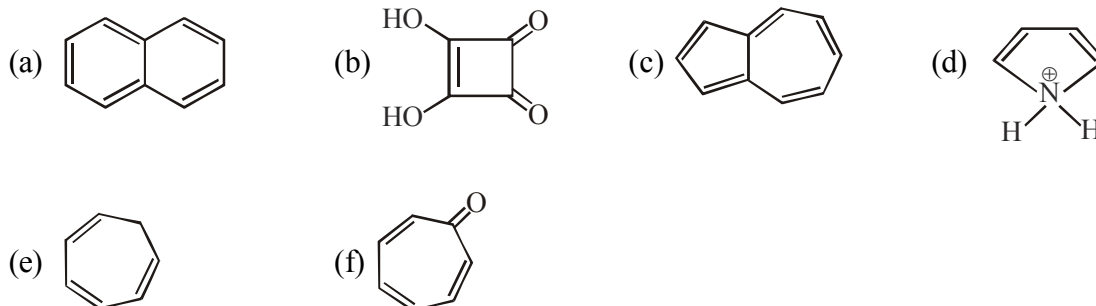
are respectively :

- (A) II, I      (B) III, IV      (C) I, II      (D) I, IV

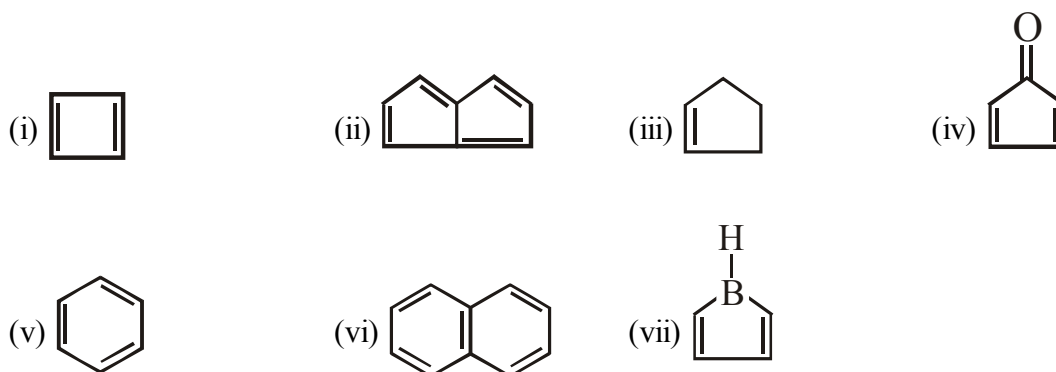
23. Most stable carbocation is formed by the heterolysis of :

- (A)  $(\text{CH}_3)_3\text{CBr}$       (B)  $(\text{C}_6\text{H}_5)_3\text{CBr}$       (C)  $(\text{C}_6\text{H}_5)_2\text{CHBr}$       (D)  $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$

24. Total number of aromatic compounds

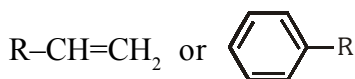


25. Identify total number of compounds which are unstable at room temperature ?



EXERCISE-IV (J-MAIN)

1. In the following benzy/allyl system [AIEEE-2002]



(R is alkyl group)

decreasing order of inductive effect is-

- (1)  $(CH_3)_3C- > (CH_3)_2CH- > CH_3CH_2-$  (2)  $CH_3-CH_2- > (CH_3)_2CH- > (CH_3)_3C-$   
 (3)  $(CH_3)_2CH- > CH_3CH_2- > (CH_3)_3CH-$  (4) None of these
2. In the anion  $HCOO^-$  the two carbon-oxygen bonds are found to be of equal length. What is the reason for it- [AIEEE-2003]

- (1) Electronic orbits of carbon atoms are hybridised  
 (2) The  $C=O$  bond is weaker than the  $C-O$  bond  
 (3) The anion  $HCOO^-$  has two resonating structure  
 (4) The anion is obtained by removal of a proton from the acid molecule

3. Which one of the following does not have  $sp^2$  hybridised carbon [AIEEE-2004]

- (1) Acetamide (2) Acetic acid (3) Acetonitrile (4) Acetone

4. Due to the presence of an unpaired electron, free radicals are - [AIEEE-2005]

- (1) Chemically inactive (2) Chemically reactive  
 (3) Cations (4) Anions

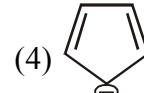
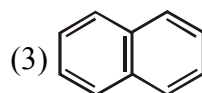
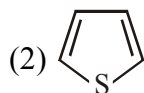
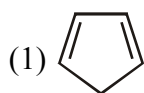
5. The increasing order of stability of the following free radicals is [AIEEE-2006]







- (1)  $(C_6H_5)_3\dot{C} < (C_6H_5)_2\dot{C}H < (CH_3)_3\dot{C} < (CH_3)_2\dot{C}H$   
 (2)  $(C_6H_5)_2\dot{C}H < (C_6H_5)_3\dot{C} < (CH_3)_3\dot{C} < (CH_3)_2\dot{C}H$   
 (3)  $(CH_3)_2\dot{C}H < (CH_3)_3\dot{C} < (C_6H_5)_3\dot{C} < (C_6H_5)_2\dot{C}H$   
 (4)  $(CH_3)_2\dot{C}H < (CH_3)_3\dot{C} < (C_6H_5)_2\dot{C}H < (C_6H_5)_3\dot{C}$

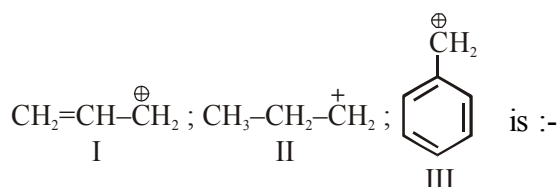
6. Arrange the carbanions,  $(CH_3)_3\bar{C}$ ,  $\bar{CCl}_3$ ,  $(CH_3)_2\bar{C}H$ ,  $C_6H_5\bar{C}H_2$ , in order of their decreasing stability [AIEEE-2009]

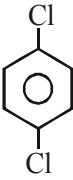
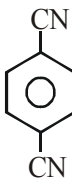
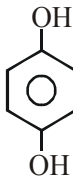
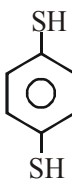



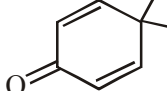
- (1)  $\bar{CCl}_3 > C_6H_5\bar{C}H_2 > (CH_3)_2\bar{C}H > (CH_3)_3\bar{C}$  (2)  $(CH_3)_3\bar{C} > (CH_3)_2\bar{C}H > C_6H_5\bar{C}H_2 > \bar{CCl}_3$   
 (3)  $C_6H_5\bar{C}H_2 > \bar{CCl}_3 > (CH_3)_3\bar{C} > (CH_3)_2\bar{C}H$  (4)  $(CH_3)_2\bar{C}H > \bar{CCl}_3 > C_6H_5\bar{C}H_2 > (CH_3)_3\bar{C}$

7. The non aromatic compound among the following is :- [AIEEE-2011]



8. ortho-Nitrophenol is less soluble in water than p- and m- Nitrophenols because :-  
 (1) Melting point of o-Nitrophenol is lower than those of m- and p- isomers [AIEEE-2012]  
 (2) o-Nitrophenol is more volatile in steam than those of m- and p- isomers  
 (3) o-Nitrophenol shows Intramolecular H-bonding  
 (4) o-Nitrophenol shows Intermolecular H-bonding
9. Which of the following compounds are antiaromatic :- [AIEEE-2012(Online)]
- (I)  (II)  (III)  (IV) 
- (V)  (VI) 
- (1) (III) and (VI) (2) (II) and (V) (3) (I) and (V) (4) (V) and (VI)
10. Among the following the molecule with the lowest dipole moment is :- [AIEEE-2012(Online)]  
 (1)  $\text{CHCl}_3$  (2)  $\text{CH}_2\text{Cl}_2$  (3)  $\text{CCl}_4$  (4)  $\text{CH}_3\text{Cl}$
11. The order of stability of the following carbocations [JEE-MAIN-2013]



- (1) III > II > I (2) II > III > I (3) I > II > III (4) III > I > II
12. For which of the following molecule significant  $\mu \neq 0$  [JEE-MAIN-2014]
- (1)  (2)  (3)  (4) 
- (1) Only (3) (2) (3) and (4) (3) Only (1) (4) (1) and (2)
13. Which of the following molecules is least resonance stabilized ? [JEE-MAIN-2017]
- (1)  (2)  (3)  (4) 

EXERCISE # V (J-ADVANCE)

1. Which one of the following has the smallest heat of hydrogenation per mole of  $H_2$  ? [IIT-93]  
 (A) 1-Butene (B) trans-2-Butene  
 (C) cis-2-Butene (D) 1, 3-Butadiene

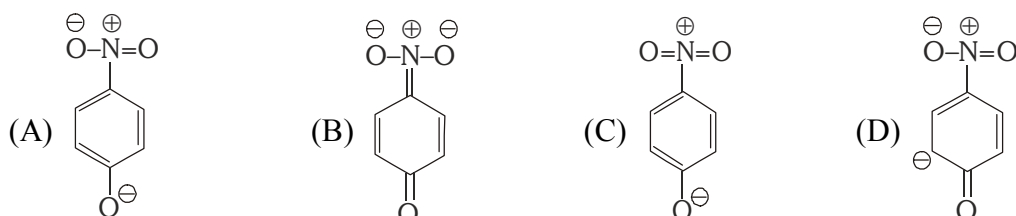
2. Most stable carbonium ion is [IIT-95]

- (A)  $p\text{-NO}_2\text{—C}_6\text{H}_4\text{—}\overset{\oplus}{\text{C}}\text{H}_2$  (B)  $\text{C}_6\text{H}_5\text{—}\overset{\oplus}{\text{C}}\text{H}_2$   
 (C)  $p\text{-Cl—C}_6\text{H}_4\text{—}\overset{\oplus}{\text{C}}\text{H}_2$  (D)  $p\text{-CH}_3\text{O—C}_6\text{H}_4\text{—}\overset{\oplus}{\text{C}}\text{H}_2$

3. Arrange the following compounds in order of increasing dipole moment : [IIT-96]  
 toluene (I) m-dichlorobenzene (II)  
 o-dichlorobenzene (III) p-dichlorobenzene (IV)

- (A)  $\text{I} < \text{IV} < \text{II} < \text{III}$  (B)  $\text{IV} < \text{I} < \text{II} < \text{III}$  (C)  $\text{IV} < \text{I} < \text{III} < \text{II}$  (D)  $\text{IV} < \text{II} < \text{I} < \text{III}$

4. The most unlikely representation of resonance structure of p-nitrophenoxide ion is - [IIT-99]



5. An aromatic molecule will not [IIT-99]  
 (A) have  $4n\pi$  electrons (B) have  $(4n + 2)\pi$  electrons  
 (C) be planar (D) be cyclic

6. **Statement-I** : p-Hydroxybenzoic acid has a lower boiling point than o-hydroxybenzoic acid.

**Because**

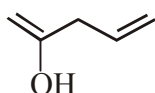
**Statement-II** : o-Hydroxybenzoic acid has intramolecular hydrogen bonding. [IIT 2003]

- (A) Statement-I is True, Statement-II is True ; Statement-II is a correct explanation for Statement-I  
 (B) Statement-I is True, Statement-II is True ; Statement-II is NOT a correct explanation for Statement-I  
 (C) Statement-I is True, Statement-II is False.  
 (D) Statement-I is False, Statement-II is True.

7. Among the following, the molecule with the highest dipole moment is [IIT-2003]

- (A)  $\text{CH}_3\text{Cl}$  (B)  $\text{CH}_2\text{Cl}_2$  (C)  $\text{CHCl}_3$  (D)  $\text{CCl}_4$

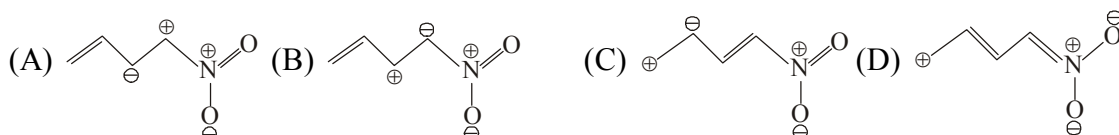
8. Give resonating structures of following compound. [IIT 2003]



9. Which of the following is least stable : [IIT-2005]

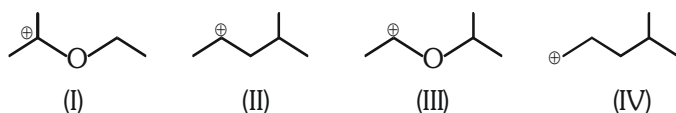
- (A)  $\text{CH}_3\text{—}\overset{\oplus}{\text{O}}\text{=CH—}\overset{\ominus}{\text{CH}}\text{—HC=CH}_2$  (B)  $\text{CH}_3\text{—}\overset{\oplus}{\text{O}}\text{=CH—CH=HC—}\overset{\ominus}{\text{CH}}_2$   
 (C)  $\text{CH}_3\text{—O—}\overset{\oplus}{\text{CH}}\text{—}\overset{\ominus}{\text{CH}}\text{—HC=CH}_2$  (D)  $\text{CH}_3\text{—O—}\overset{\ominus}{\text{CH}}\text{—}\overset{\oplus}{\text{CH}}\text{—CH=CH}_2$

10. Among the following, the least stable resonance structure is - [IIT-2007]



11. The correct stability order for the following species is :

[IIT-2008]



- (A) II > IV > I > III (B) I > II > III > IV (C) II > I > IV > III (D) I > III > II > IV

12. The correct stability order of the following resonance structures is

[IIT-2009]



- (A) (I) > (II) > (IV) > (III)

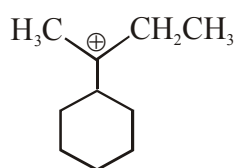
- (B) (I) > (III) > (II) > (IV)

- (C) (II) > (I) > (III) > (IV)

- (D) (III) > (I) > (IV) > (II)

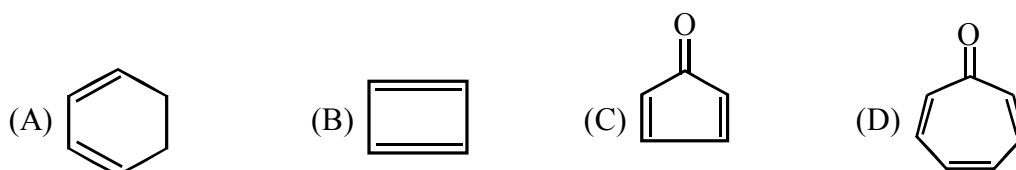
13. The total number of contributing structures showing hyperconjugation (involving C-H bonds) for the following carbocation is.

[IIT-2011]



14. Which of the following molecules, in pure form, is (are) **unstable** at room temperature ?

[IIT-2012]



15. The hyperconjugative stabilities of tert-butyl cation and 2-butene, respectively, are due to

[IIT-2013]

- (A)  $\sigma \rightarrow p$  (empty) and  $\sigma \rightarrow \pi$  electron delocalisations

- (B)  $\sigma \rightarrow \sigma$  and  $\sigma \rightarrow \pi$  electron delocalisations

- (C)  $\sigma \rightarrow p$  (filled) and  $\sigma \rightarrow \pi$  electron delocalisations

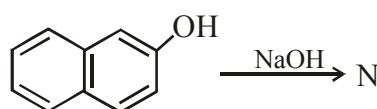
- (D)  $p$  (filled)  $\rightarrow \sigma$  and  $\sigma \rightarrow \pi$  electron delocalisations

16. The total number of lone-pairs of electrons in melamine is

[IIT-2013]

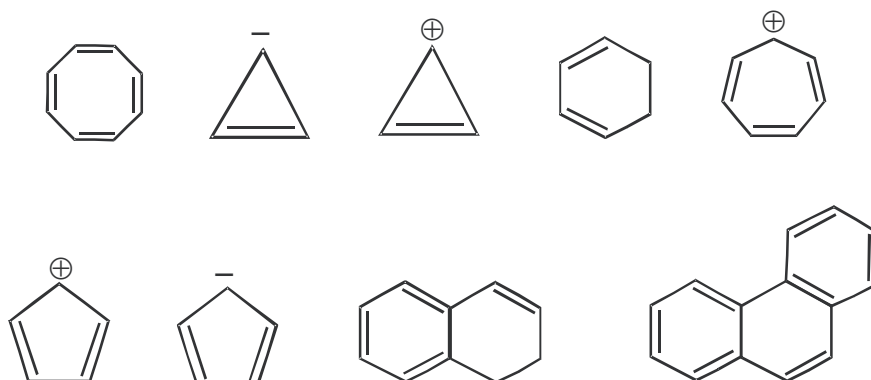
17. The number of resonance structures for N is :

[IIT-2015]



18. Among the following, the number of aromatic compound (s) is-

[JEE - Adv. 2017]

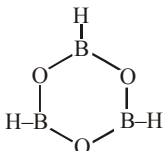
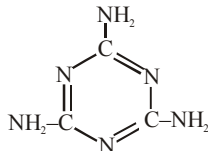
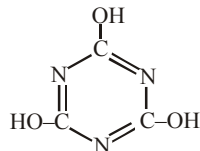


# ANSWER KEY

## EXERCISE # I

1. (D)      2. (C)      3. (B)      4. (A,B,D)      5. 4(b, d, f, g)
6. (a), (c), (d), (g), (j), (l), (m)      7. (A)      8. (A)      9. (A)
10. A,D      11. (D)      12. b, d, e      13. b d e      14. (d)      15. c, f
16. a, b, c, d, f      17. b, c, f      18.      19. a-I, b-II, c-II, d-II, e-I
20. a-I, b-I, c-I, d-I, e-II, f-II      21. a, e, f, g
22. (a) Resonance forms, (b) A, (c) C, (d) A & B, (e) B & C, (f) 0, (g) B, (h) B
23. (a) II; (b) II; (c) II      24. (A)      25. a-II, b-II, c-II, d-II      26. a & b
27. (i)-I, (ii)-II, (iii)-II, (iv)-I, (v)-I, (vi)-II, (vii)-I, (viii)-II, (ix)-II, (x)-II, (xi)-II, (xii)-I, (xiii)-I, (xiv)-I, (xv)-I
28. a-II, b-I, c-I, d-II, e-I      29. (B)      30. (D)      31. (B)      32. (C)
33. (C)      34. (C)      35. (D)      36. (A,B,C)
37. (B)      38. (B)      39. (C)      40. (D)      41. (D)      42. (A)
43. (B,C,D)      44. (B)      45. (A)      46. (A,C,D)
47. a-I, b-I, c-II, d-I, e-I, f-I      48. a-II, b-I, c-I, d-I, e-II, f-II      49. (D)
50. C > B > A      51. (A)

## EXERCISE # II

1. (i) a, b; (ii) a, c; (iii) b, c, d; (iv) a, b, c, d, e, f
2. Aromatic → a, b, d, e, g; Non-aromatic → c, f      3. (C)      4. (C)      5. (B)
6. (A)      7. (a)  (b)  (c) 
8. (D)
9. (i) c > b > a      (ii) c > b > a      (iii) b > c > a      (iv) d > c > b > a      (v) c > b > a  
 (vi) b > c > a      (vii) c > b > a      (viii) c > a > d > b      (ix) b > c > a      (x) c > a > b  
 (xi) c > a > b      (xii) a > b > c > d      (xiii) b > a > c > d      (xiv) d > e > b > a > c  
 (xv) a > c > b      (xvi) b > c > a
10. (C)      11. (a) I; (b) I; (c) II; (d) II;      12. (C)      13. (A)      14. (A)
15. (D)      16. (B)



17. (i)  $a < b$  (ii)  $d < a < c < b$  (iii)  $b < a$  (iv)  $c < b < a$  (v)  $c < a < b$  (vi)  $a < c < b$   
 (vii)  $c < b < a$  (viii)  $c < b < a$  (ix)  $b < a$  (x)  $a < c < b < d$  18. (A)
19. (D) 20. (B) 21. (D)
22. (a)  $IV < I < II < III < V$  (b)  $III < IV < I < II$  23. (B) 24. (A)
25. (a) -I ; (b) -I ; (c) -II 26. (a) 4658 ; (b) 4638 (c) 4632 ; (d) 4650 ; (e) 5293
27. (A) 28. (B) 29. (D)
30. (i)  $d > c > b > a$  ; (ii)  $e > c > d > b > a$  ; (iii)  $b > a$  (iv)  $a > b$  (v)  $b > a$  ; (vi)  $a > b$
31. (i)  $a < b$  ; (ii)  $e < d < c < b < a$  ; (iii)  $a < c < b$  ; (iv)  $a > b > c$
32. (i)  $c > b > a$  ; (ii)  $a > b > c > d$  ; (iii)  $a > b$  ; (iv)  $c > b > a$
33. a - I ; b - I ; c - II, d - I 34. Stability order :  $d > c > b > a$  ; HOH order :  $a > b > c > d$
35. (C) 36. (D) 37. (B) 38. (C)
39. (i)  $c > b > a$  (ii)  $a > b > c$  (iii)  $a > b$

## EXERCISE # III

1. (C) 2. (A,D) 3. (D) 4. (C) 5. (A,B,D)
6. (A)-P,S ; (B)-Q,R ; (C)-Q,S ; (D)-P,S
7. (A)  $\rightarrow$  P, Q, S ; (B)  $\rightarrow$  R ; (C)  $\rightarrow$  P, S ; (D)  $\rightarrow$  Q, S
8. (A)-R ; (B)-S ; (C)-P, T ; (D)-Q 9. (A)-Q,S ; (B)-P,S ; (C)-P,S ; (D)-R,S
10. (D) 11. (A) 12. (D) 13. (A) 14. (A) 15. (B)
16. (D) 17. (C) 18. (C) 19. (B) 20. (C) 21. (C)
22. (D) 23. (B) 24. (4) 25. (4)

## EXERCISE # IV (J-MAIN)

1. (1) 2. (3) 3. (3) 4. (2) 5. (4) 6. (1)
7. (1) 8. (3) 9. (4) 10. (3) 11. (4) 12. (2)
13. (4)

## EXERCISE # V (J-ADVANCE)

1. (D) 2. (D) 3. (B) 4. (C) 5. (A) 6. (D)
7. (A) 9. (D) 10. (A) 11. (D) 12. (B) 13. (6)
14. (B,C) 15. (A) 16. (6) 17. (9) 18. (5)





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**ALLEN**  
Session 2019-20

## SALT ANALYSIS

Analysis always does not mean breaking of substance into its ultimate constituents. Finding out the nature of substance and identity of its constituents is also analysis and is known as **qualitative analysis**.

Qualitative analysis of inorganic salts means the identification of cations and anions present in the salt or a mixture of salts. Inorganic salts may be obtained by complete or partial neutralisation of acid with base or vice-versa. In the formation of a salt, the part contributed by the **acid** is called **anion** and the part contributed by the **base** is called **cation**. For example, in the salts  $\text{CuSO}_4$  and  $\text{NaCl}$ ,  $\text{Cu}^{2+}$  and  $\text{Na}^+$  ions are cations and  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  ions are anions. Qualitative analysis is carried out on various scales. Amount of substance employed in these is different. In macro analysis, 0.1 to 0.5 g of substance and about 20 mL of solution is used. For semimicro analysis, 0.05 g substance and 1 mL solution is needed while for micro analysis amount required is very small. Qualitative analysis is carried out through the reactions which are easily perceptible to our senses such as sight and smell. Such reactions involve:

- (a) Formation of a precipitate
- (b) Change in colour
- (c) Evolution of gas etc.

Systematic analysis of an inorganic salt involves the following steps:

- (i) Preliminary examination of solid salt and its solution.
- (ii) Determination of anions by reactions carried out in solution (wet tests) and confirmatory tests.
- (iii) Determination of cations by reactions carried out in solution (wet tests) and confirmatory tests.

Although these tests are not conclusive but sometimes they give quite important clues for the presence of certain anions or cations. These tests can be performed within  $10^{-15}$  minutes. These involve noting the general appearance and physical properties, such as colour, smell, solubility etc. of the salt. These are named as **dry tests**.

**Heating of dry salt, blow pipe test, flame tests, borax bead test, sodium carbonate bead test, charcoal cavity test etc. come under dry tests.**

Solubility of a salt in water and the pH of aqueous solutions give important information about the nature of ions present in the salt. If a solution of the salt is acidic or basic in nature, this means that it is being hydrolysed in water. If the solution is basic in nature then salt may be some carbonate or sulphide etc. If the solution shows acidic nature then it may be an acid salt or salt of weak base and strong acid. In this case it is best to neutralise the solution with sodium carbonate before testing it for anions.

Gases evolved in the preliminary tests with dil.  $\text{H}_2\text{SO}_4$ /dil.  $\text{HCl}$  and conc.  $\text{H}_2\text{SO}_4$  also give good indication about the presence of acid radicals (See Tables 1 and 3). **Preliminary tests should always be performed before starting the confirmatory tests for the ions.**

**EXPERIMENT 1.1****Aim**

To detect one cation and one anion in the given salt from the following ions:

Cations -  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{As}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{NH}_4^+$

Anions -  $\text{CO}_3^{2-}$ ,  $\text{S}^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{CH}_3\text{COO}^-$ .

(Insoluble salts to be excluded)

**Theory**

Two basic principles of great use in the analysis are:

- (i) the Solubility product
- (ii) the Common ion effect.

When ionic product of a salt exceeds its solubility product, precipitation takes place. Ionic product of salt is controlled by making use of common ion effect.

**Material Required**

- Boiling tube : As per need
- Test tubes : As per requirement
- Measuring cylinder : One
- Test tube stand : One
- Test tube holder : One
- Delivery tube : One
- Corks : As per need
- Filter paper : As per need
- Reagents : As per need

**Step - I :** Preliminary Test with Dilute Sulphuric Acid → In this test the action of dilute sulphuric acid (procedure is given below) on the salt is noted at room temperature and on warming.

Carbonate ( $\text{CO}_3^{2-}$ ), sulphide ( $\text{S}^{2-}$ ), sulphite ( $\text{SO}_3^{2-}$ ), nitrite ( $\text{NO}_2^-$ ) and acetate ( $\text{CH}_3\text{COO}^-$ ) react with dilute sulphuric acid to evolve different gases. Study of the characteristics of the gases evolved gives information about the anions. Summary of characteristic properties of gases is given in Table 1.

**Procedure**

(a) Take 0.1 g of the salt in a test tube and add 1–2 mL of dilute sulphuric acid. Observe the change, if any, at room temperature. If no gas is evolved, warm the content of the test tube. If gas is evolved test it by using the apparatus shown in Fig.1 and identify the gas evolved (See Table 1).

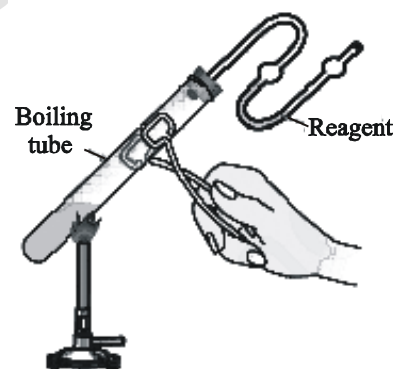


Fig. 7.1 - Testing a gas

Table 1 : Preliminary test with dilute sulphuric acid

| Observations                                                                                                         | Inference                        |                                        |
|----------------------------------------------------------------------------------------------------------------------|----------------------------------|----------------------------------------|
|                                                                                                                      | Gas Evolved                      | Possible Anion                         |
| A colourless, odourless gas is evolved with brisk effervescence, which turns lime water milky.                       | $\text{CO}_2$                    | Carbonate ( $\text{CO}_3^{2-}$ )       |
| Colourless gas with the smell of rotten eggs is evolved which turns lead acetate paper black.                        | $\text{H}_2\text{S}$             | Sulphide ( $\text{S}^{2-}$ )           |
| Colourless gas with a pungent smell, like burning sulphur which turns acidified potassium dichromate solution green. | $\text{SO}_2$                    | Sulphite ( $\text{SO}_3^{2-}$ )        |
| Brown fumes which turn acidified potassium iodide solution containing starch solution blue.                          | $\text{NO}_2$                    | Nitrite ( $\text{NO}_2^-$ )            |
| Colourless vapours with smell of vinegar. Vapours turn blue litmus red.                                              | $\text{CH}_3\text{COOH}$ vapours | Acetate, ( $\text{CH}_3\text{COO}^-$ ) |

**Confirmatory tests for  $\text{CO}_3^{2-}$ ,  $\text{S}^{2-}$ ,  $\text{SO}_3^{2-}$ ,  $\text{NO}_2^-$  and  $\text{CH}_3\text{COO}^-$**

**Confirmatory (wet) tests for anions are performed by using water extract when salt is soluble in water and by using sodium carbonate extract when salt is insoluble in water.** Confirmation of  $\text{CO}_3^{2-}$  is done by using aqueous solution of the salt or by using solid salt as such because sodium carbonate extract contains carbonate ions. Water extract is made by dissolving salt in water. Preparation of sodium carbonate extract is given below.

#### Preparation of sodium carbonate extract

**Take 1 g of salt in a porcelain dish or boiling tube. Mix about 3 g of solid sodium carbonate and add 15 mL of distilled water to it. Stir and boil the content for about 10 minutes. Cool, filter and collect the filtrate in a test tube and label it as sodium carbonate extract.**

Confirmatory tests for acid radicals, which react with dilute sulphuric acid are given in Table 2.



Table 2 : Confirmatory tests for  $\text{CO}_3^{2-}$ ,  $\text{S}^{2-}$ ,  $\text{SO}_3^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{CH}_3\text{COO}^-$ 

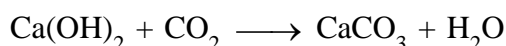
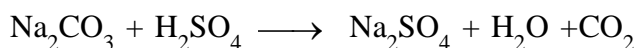
| Anion                                  | Confirmatory Test                                                                                                                                                                                                                                                                                                                                                                                                                                    |
|----------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Carbonate ( $\text{CO}_3^{2-}$ )       | Take 0.1 g of salt in a test tube, add dilute sulphuric acid. $\text{CO}_2$ gas is evolved with brisk effervescence which turns lime water milky. On passing the gas for some more time, milkiness disappears.                                                                                                                                                                                                                                       |
| Sulphide ( $\text{S}^{2-}$ )           | Take 1 mL of water extract and make it alkaline by adding ammonium hydroxide or sodium carbonate extract. Add a drop of sodium nitroprusside solution. Purple or violet colouration appears.                                                                                                                                                                                                                                                         |
| Sulphite ( $\text{SO}_3^{2-}$ )        | (a) Take 1 mL of water extract or sodium carbonate extract in a test tube and add barium chloride solution. A white precipitate is formed which dissolves in dilute hydrochloric acid and sulphur dioxide gas is also evolved<br>(b) Take the precipitate of step (a) in a test tube and add a few drops of potassium permanganate solution acidified with dil. $\text{H}_2\text{SO}_4$ . Colour of potassium permanganate solution gets discharged. |
| Nitrite ( $\text{NO}_2^-$ )            | (a) Take 1 mL of water extract in a test tube. Add a few drops of potassium iodide solution and a few drops of starch solution, acidify with acetic acid. Blue colour appears.<br>(b) Acidify 1 mL of water extract with acetic acid. Add 2-3 drops of sulphanilic acid solution followed by 2-3 drops of 1-naphthylamine reagent. Appearance of red colour indicates the presence of nitrite ion.                                                   |
| Acetate, ( $\text{CH}_3\text{COO}^-$ ) | (a) Take 0.1 g of salt in a china dish. Add 1 mL of ethanol and 0.2 mL conc. $\text{H}_2\text{SO}_4$ and heat. Fruity odour confirms the presence of acetate ion.<br>(b) Take 0.1 g of salt in a test tube, add 1-2 mL distilled water, shake well filter if necessary. Add 1 to 2 mL neutral ferric chloride solution to the filtrate. Deep red colour appears which disappears on boiling and a brown-red precipitate is formed.                   |

### Chemistry of Confirmatory Tests

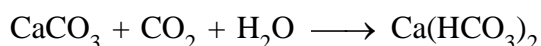
#### 1. Test for Carbonate ion [ $\text{CO}_3^{2-}$ ]

If there is effervescence with the evolution of a colourless and odourless gas on adding dil.  $\text{H}_2\text{SO}_4$  to the solid salt, this indicates the presence of carbonate ion.

The gas turns lime water milky due to the formation of  $\text{CaCO}_3$

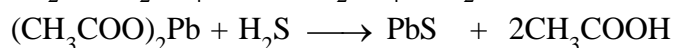
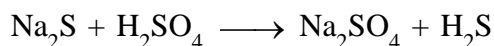


If  $\text{CO}_2$  gas is passed in excess through lime water, the milkiness disappears due to the formation of calcium hydrogen carbonate which is soluble in water.



## 2. Test for Sulphide ion [S<sup>2-</sup>]

(a) With warm dilute H<sub>2</sub>SO<sub>4</sub> a sulphide gives hydrogen sulphide gas which smells like rotten eggs. A piece of filter paper dipped in lead acetate solution turns black on exposure to the gas due to the formation of lead sulphide which is black in colour.



Lead sulphide

Black precipitate

(b) If the salt is soluble in water, take the solution of salt in water make it alkaline with ammonium hydroxide and add sodium nitroprusside solution. If it is insoluble in water take sodium carbonate extract and add a few drops of sodium nitroprusside solution. Purple or violet colouration due to the formation of complex compound Na<sub>4</sub>[Fe(CN)<sub>5</sub>NOS] confirms the presence of sulphide ion in the salt.

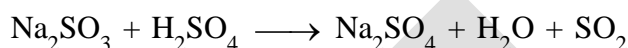


Sodium nitroprusside

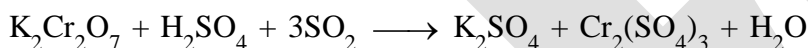
Complex of Purple colour

## 3. Test for Sulphite ion [SO<sub>3</sub><sup>2-</sup>]

(a) On treating sulphite with warm dil. H<sub>2</sub>SO<sub>4</sub>, SO<sub>2</sub> gas is evolved which is suffocating with the smell of burning sulphur.



The gas turns potassium dichromate paper acidified with dil. H<sub>2</sub>SO<sub>4</sub>, green.



Chromium

sulphate (green)

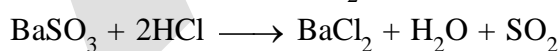
(b) An aqueous solution or sodium carbonate extract of the salt produces a white precipitate of barium sulphite on addition of barium chloride solution.



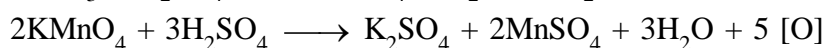
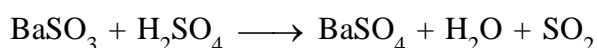
White ppt.

This precipitate gives following tests.

- (i) This precipitate on treatment with dilute HCl, dissolves due to decomposition of sulphite by dilute HCl. Evolved SO<sub>2</sub> gas can be tested.

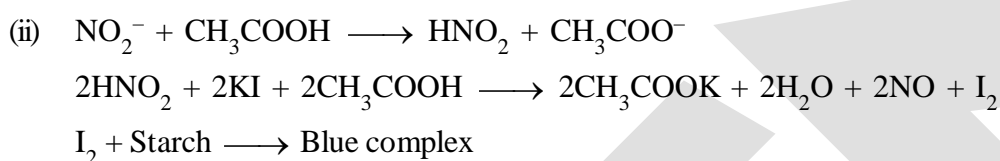
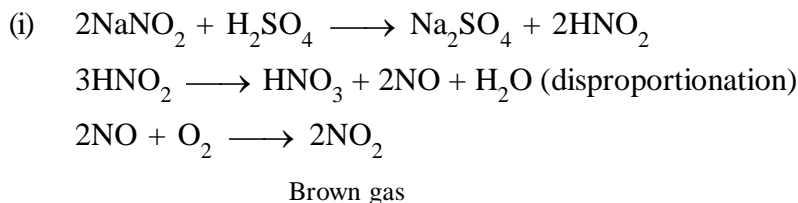


- (ii) Precipitate of sulphite decolourises acidified potassium permanganate solution.

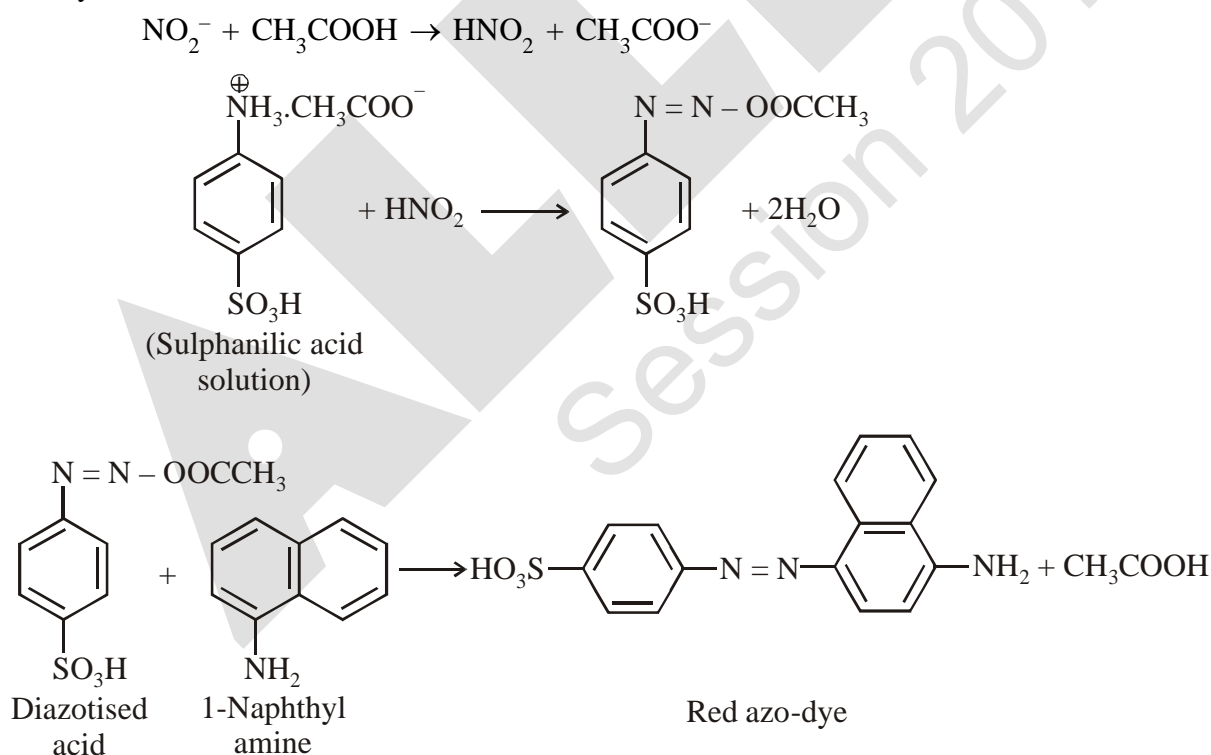


#### 4. Test for Nitrite ion $[\text{NO}_2^-]$

- (a) On treating a solid nitrite with dil.  $\text{H}_2\text{SO}_4$  and warming, reddish brown fumes of  $\text{NO}_2$  gas are evolved. Addition of potassium iodide solution to the salt solution followed by freshly prepared starch solution and acidification with acetic acid produces blue colour. Alternatively, a filter paper moistened with potassium iodide and starch solution and a few drops of acetic acid turns blue on exposure to the gas, due to the interaction of liberated iodine with starch.



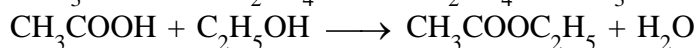
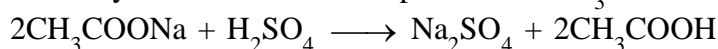
- (b) **Sulphanilic acid — 1-naphthylamine reagent test (Griess-Ilosvay test) :** On adding sulphanilic acid and 1-naphthylamine reagent to the water extract or acidified with acetic acid, sulphanilic acid is diazotised in the reaction by nitrous acid formed. Diazotised acid couples with 1-naphthylamine to form a red azo-dye.



*The test solution should be very dilute. In concentrated solutions reaction does not proceed beyond diazotisation.*

### 5. Test for Acetate ion $[\text{CH}_3\text{COO}^-]$

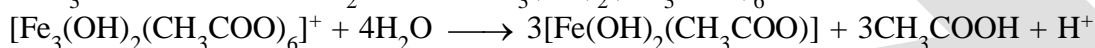
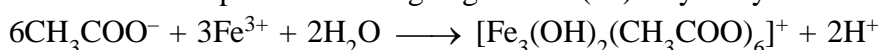
- (a) If the salt smells like vinegar on treatment with dil.  $\text{H}_2\text{SO}_4$ , this indicates the presence of acetate ions. Take 0.1 g of salt in a china dish and add 1 mL of ethanol. Then add about 0.2 mL of conc.  $\text{H}_2\text{SO}_4$  and heat. Fruity odour of ethyl acetate indicates the presence of  $\text{CH}_3\text{COO}^-$  ion.



Ethylacetate

(Fruity odour)

- (b) Acetate gives deep red colour on reaction with neutral ferric chloride solution due to the formation of complex ion which decomposes on heating to give Iron (III) dihydroxyacetate as brown red precipitate.



Iron(III)dihydroxyacetate

(Brown-red precipitate)

**Step-II : Preliminary Test with Concentrated Sulphuric Acid** If no positive result is obtained from dil.  $\text{H}_2\text{SO}_4$  test, take 0.1 g of salt in a test tube and 3-4 drops of conc.  $\text{H}_2\text{SO}_4$ . Observe the change in the reaction mixture in cold and then warm it. Identify the gas evolved on heating (see Table 3).

**Table 3 : Preliminary examination with concentrated sulphuric acid**

| Observations                                                                                                                                                                                                             | Inference             |                                          |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|------------------------------------------|
|                                                                                                                                                                                                                          | Gas/Vapours Evolved   | Possible Anion                           |
| A colourless gas with pungent smell, which gives dense white fumes when a rod dipped in ammonium hydroxide is brought near the mouth of the test tube.                                                                   | HCl                   | Chloride, ( $\text{Cl}^-$ )              |
| Reddish brown gas with a pungent odour is evolved. Intensity of reddish gas increases on heating the reaction mixture after addition of solid $\text{MnO}_2$ to the reaction mixture. Solution also acquires red colour. | $\text{Br}_2$ vapours | Bromide, ( $\text{Br}^-$ )               |
| Violet vapours, which turn starch paper blue and a layer of violet sublimate is formed on the sides of the tube. Fumes become dense on adding $\text{MnO}_2$ to the reaction mixture.                                    | $\text{I}_2$ vapours  | Iodide, ( $\text{I}^-$ )                 |
| Brown fumes evolve which become dense upon heating the reaction mixture after addition of copper turnings and the solution acquires blue colour.                                                                         | $\text{NO}_2$         | Nitrate, ( $\text{NO}_3^-$ )             |
| Colourless, odourless gas is evolved which turns lime water milky and the gas coming out of lime water burns with a blue flame, if ignited.                                                                              | CO and $\text{CO}_2$  | Oxalate, ( $\text{C}_2\text{O}_4^{2-}$ ) |

**Table 4 : Confirmatory tests for  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$  and  $\text{C}_2\text{O}_4^{2-}$**

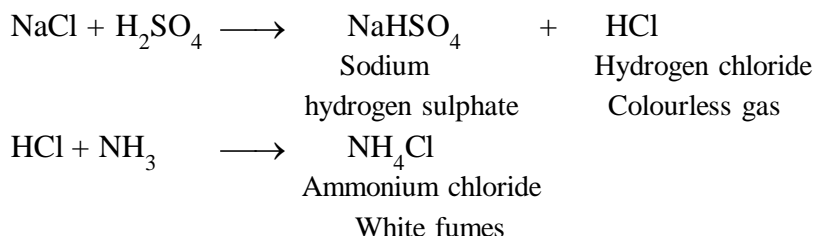
| Anion                      | Confirmatory Test                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |
|----------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Chloride ( $\text{Cl}^-$ ) | <p>(a) Take 0.1 g of salt in a test tube, add a pinch of manganese dioxide and 3-4 drops of conc. sulphuric acid. Heat the reaction mixture. Greenish yellow chlorine gas is evolved which is detected by its pungent odour and bleaching action.</p> <p>(b) Take 1 mL of sodium carbonate extract in a test tube, acidify it with dil. <math>\text{HNO}_3</math> or take water extract and add silver nitrate solution. A curdy white precipitate is obtained which is soluble in ammonium hydroxide solution.</p> <p>(c) Take 0.1 g salt and a pinch of solid potassium dichromate in a test tube, add conc. <math>\text{H}_2\text{SO}_4</math>, heat and pass the gas evolved through sodium hydroxide solution. It becomes yellow. Divide the solution into two parts. Acidify one part with acetic acid and add lead acetate solution. A yellow precipitate is formed. Acidify the second part with dilute sulphuric acid and add 1 mL of amyl alcohol followed by 1 mL of 10% hydrogen peroxide. After gentle shaking the organic layer turns blue.</p> |
| Bromide ( $\text{Br}^-$ )  | <p>(a) Take 0.1 g of salt and a pinch of <math>\text{MnO}_2</math> in a test tube. Add 3-4 drops conc. sulphuric acid and heat. Intense brown fumes are evolved.</p> <p>(b) Neutralise 1 mL of sodium carbonate extract with hydrochloric acid (or take the water extract). Add 1 mL carbon tetrachloride (<math>\text{CCl}_4</math>)/chloroform (<math>\text{CHCl}_3</math>)/carbon disulphide. Now add an excess of chlorine water dropwise and shake the test tube. A brown colouration in the organic layer confirms the presence of bromide ion.</p> <p>(c) Acidify 1 mL of sodium carbonate extract with dil. <math>\text{HNO}_3</math> (or take 1 mL water extract) and add silver nitrate solution. A pale yellow precipitate soluble with difficulty in ammonium hydroxide solution is obtained.</p>                                                                                                                                                                                                                                                 |
| Iodide ( $\text{I}^-$ )    | <p>(a) Take 1 mL of salt solution neutralised with HCl and add 1 mL chloroform/carbon tetrachloride/carbon disulphide. Now add an excess of chlorine water drop wise and shake the test tube. A violet colour appears in the organic layer.</p> <p>(b) Take 1 mL of sodium carbonate extract acidify it with dil. <math>\text{HNO}_3</math> (or take water extract). Add, silver nitrate solution. A yellow precipitate insoluble in <math>\text{NH}_4\text{OH}</math> solution is obtained.</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |

| Anion                                   | Confirmatory Test                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |
|-----------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| *Nitrate ( $\text{NO}_3^-$ )            | Take 1 mL of salt solution in water in a test tube. Add 2 mL of conc. $\text{H}_2\text{SO}_4$ and mix thoroughly. Cool the mixture under the tap. Add freshly prepared ferrous sulphate along the sides of the test tube without shaking. A dark brown ring is formed at the junction of the two solutions.                                                                                                                                                                                                                                                                                            |
| Oxalate ( $\text{C}_2\text{O}_4^{2-}$ ) | <p>(a) Take 1 mL of water extract or sodium carbonate extract acidified with acetic acid and add calcium chloride solution. A white precipitate insoluble in ammonium oxalate and oxalic acid solution but soluble in dilute hydrochloric acid and dilute nitric acid is formed.</p> <p>(b) Take the precipitate from test (a) and dissolve it in dilute <math>\text{H}_2\text{SO}_4</math>. Add very dilute solution of <math>\text{KMnO}_4</math> and warm. Colour of <math>\text{KMnO}_4</math> solution is discharged. Pass the gas coming out through lime water. The lime water turns milky.</p> |

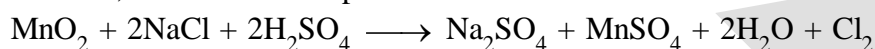
## Chemistry of Confirmatory Tests

### 1. Test for Chloride ion $[Cl^-]$

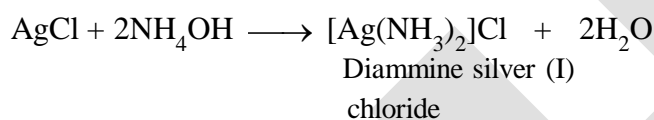
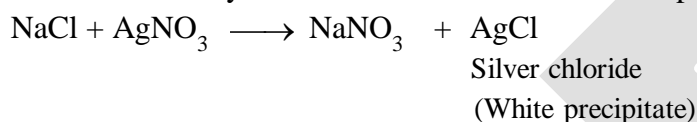
(a) If on treatment with warm conc.  $H_2SO_4$  the salt gives a colourless gas with pungent smell or if the gas which gives dense white fumes with ammonia solution, then the salt may contain  $Cl^-$  ions and the following reaction occurs.



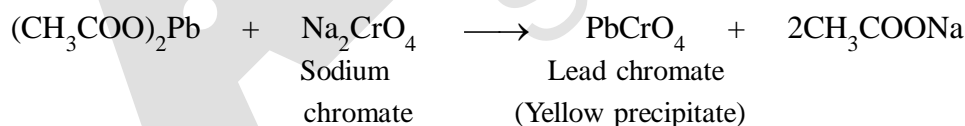
(b) If a salt gives effervescence on heating with conc.  $H_2SO_4$  and  $MnO_2$  and a light greenish yellow pungent gas is evolved, this indicates the presence of  $Cl^-$  ions.



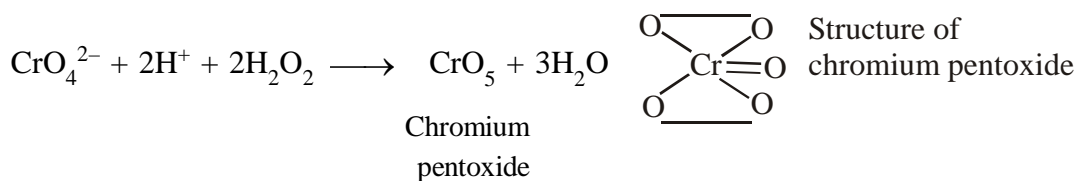
(c) Salt solution acidified with dilute  $HNO_3$  on addition of silver nitrate solution gives a curdy white precipitate soluble in ammonium hydroxide solution. This indicates the presence of  $Cl^-$  ions in the salt.



(d) Mix a little amount of salt and an equal amount of solid potassium dichromate ( $K_2Cr_2O_7$ ) in a test tube and add conc.  $H_2SO_4$  to it. Heat the test tube and pass the evolved gas through sodium hydroxide solution. If a yellow solution is obtained, divide the solution into two parts. Acidify the first part with acetic acid and then add lead acetate solution. Formation of a yellow precipitate of lead chromate confirms the presence of chloride ions in the salt. This test is called **chromyl chloride test**.

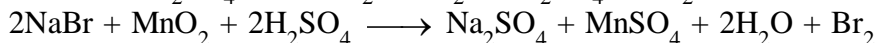
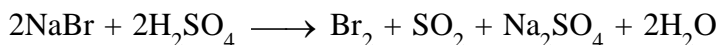


Acidify the second part with dilute sulphuric acid and add small amounts of amyl alcohol and then 1 mL of 10% hydrogen peroxide solution. On gentle shaking organic layer turns blue.  $CrO_4^{2-}$  ion formed in the reaction of chromyl chloride with sodium hydroxide reacts with hydrogen peroxide to form chromium pentoxide ( $CrO_5$ ) (See structure) which dissolves in amyl alcohol to give blue colour.

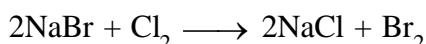


**2. Test for Bromide ion ( $\text{Br}^-$ )**

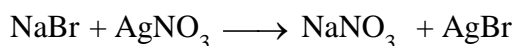
If on heating the salt with conc.  $\text{H}_2\text{SO}_4$  reddish brown fumes of bromine are evolved in excess, this indicates the presence of  $\text{Br}^-$  ions. The fumes get intensified on addition of  $\text{MnO}_2$ . Bromine vapours turn starch paper yellow.



(a) Add 1 mL of carbon tetrachloride ( $\text{CCl}_4$ )/chloroform ( $\text{CHCl}_3$ ) and excess of freshly prepared chlorine water dropwise to the salt solution in water or sodium carbonate extract neutralised with dilute  $\text{HCl}$ . Shake the test tube vigorously. The appearance of an orange brown colouration in the organic layer due to the dissolution of bromine in it, confirms the presence of bromide ions.



(b) Acidify the sodium carbonate extract of the salt with dil.  $\text{HNO}_3$ . Add silver nitrate ( $\text{AgNO}_3$ ) solution and shake the test tube. A pale yellow precipitate is obtained which dissolves in ammonium hydroxide with difficulty.

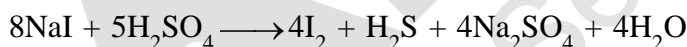
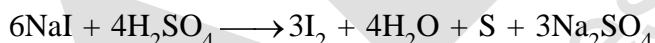
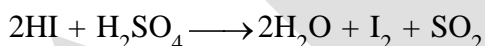
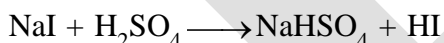
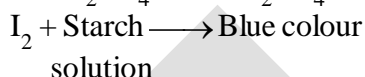
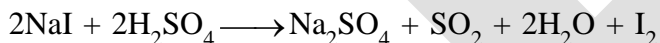


Silver bromide

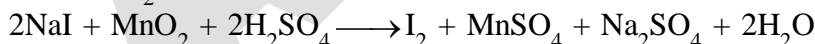
Pale yellow precipitate

**3. Test for Iodide ion ( $\text{I}^-$ )**

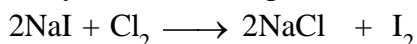
(a) If on heating the salt with conc.  $\text{H}_2\text{SO}_4$ , deep violet vapours with a pungent smell are evolved. These turns starch paper blue and a violet sublimate is formed on the sides of the test tube, it indicates the presence of  $\text{I}^-$  ions. Some  $\text{HI}$ , sulphur dioxide, hydrogen sulphide, and sulphur are also formed due to the following reactions.



On adding  $\text{MnO}_2$  to the reaction mixture, the violet vapours become dense.

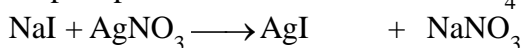


(b) Add 1 mL of  $\text{CHCl}_3$  or  $\text{CCl}_4$  and chlorine water in excess to the salt solution in water or sodium carbonate extract neutralised with dil.  $\text{HCl}$  and shake the test tube vigorously. Presence of violet colouration in the organic layer confirms the presence of iodide ions.



Iodine dissolves in the organic solvent and the solution becomes violet.

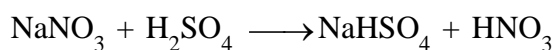
(c) Acidify sodium carbonate extract of the salt with dil.  $\text{HNO}_3$  and add  $\text{AgNO}_3$  solution. Appearance of a yellow precipitate insoluble in excess of  $\text{NH}_4\text{OH}$  confirms the presence of iodide ions.



silver iodide

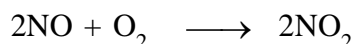
(Yellow precipitate)

(a) If on heating the salt with conc.  $\text{H}_2\text{SO}_4$  light brown fumes are evolved then heat a small quantity of the given salt with few copper turnings or chips and conc.  $\text{H}_2\text{SO}_4$ . Evolution of excess of brown fumes indicates the presence of nitrate ions. The solution turns blue due to the formation of copper sulphate.



Copper sulphate

(Blue)

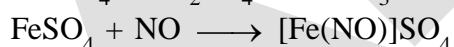
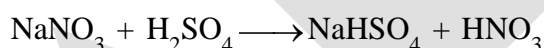


(Brown fumes)

(b) Take 1 mL of an aqueous solution of the salt and add 2 mL conc.  $\text{H}_2\text{SO}_4$  slowly. Mix the solutions thoroughly and cool the test tube under the tap. Now, add freshly prepared ferrous sulphate solution along the sides of the test tube dropwise so that it forms a layer on the top of the liquid already present in the test tube. A dark brown ring is formed at the junction of the two solutions due to the formation of nitroso ferrous sulphate (Fig. 1.2). Alternatively first ferrous sulphate is added and then concentrated sulphuric acid is added.



Fig. 1.2 : Formation of brown ring

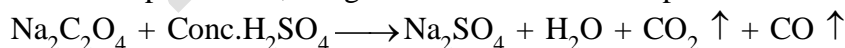


Nitroso ferrous sulphate

(Brown)

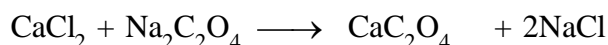
## 5. Test for Oxalate ion $[\text{C}_2\text{O}_4^{2-}]$

If carbon dioxide gas along with carbon monoxide gas is evolved in the preliminary examination with concentrated sulphuric acid, this gives indication about the presence of oxalate ion.



Oxalate is confirmed by the following tests:

(a) Acidify sodium carbonate extract with acetic acid and add calcium chloride solution. A white precipitate of calcium oxalate, insoluble in ammonium oxalate and oxalic acid solution indicates the presence of oxalate ion.



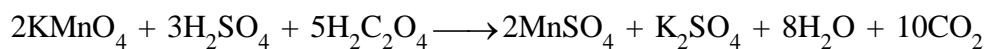
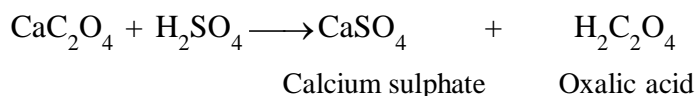
Calcium oxalate

(White precipitate)



**(b)  $\text{KMnO}_4$  test**

Filter the precipitate from test (a). Add dil.  $\text{H}_2\text{SO}_4$  to it followed by dilute  $\text{KMnO}_4$  solution and warm. Pink colour of  $\text{KMnO}_4$  is discharged:



Pass the gas evolved through lime water. A white precipitate is formed which dissolves on passing the gas for some more time.

**Step-III : Test for Sulphate and Phosphate**

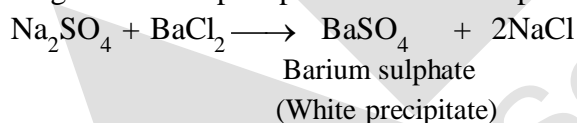
If no positive test is obtained in Steps-I and II, then tests for the presence of sulphate and phosphate ions are performed. These tests are summarised in Table 5.

**Table 5 : Confirmatory tests for Sulphate and Phosphate**

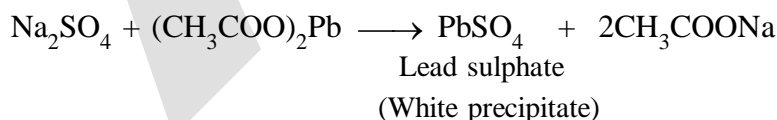
| Ion                              | Confirmatory Test                                                                                                                                                                                                                                                                                                                                                                                                                             |
|----------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Sulphate ( $\text{SO}_4^{2-}$ )  | (a) Take 1 mL water extract of the salt in water or sodium carbonate and after acidifying with dilute hydrochloric acid add $\text{BaCl}_2$ solution. White precipitate insoluble in conc. $\text{HCl}$ or conc. $\text{HNO}_3$ is obtained.<br>(b) Acidify the aqueous solution or sodium carbonate extract with acetic acid and add lead acetate solution. Appearance of white precipitate confirms the presence of $\text{SO}_4^{2-}$ ion. |
| Phosphate ( $\text{PO}_4^{3-}$ ) | (a) Acidify sodium carbonate extract or the solution of the salt in water with conc. $\text{HNO}_3$ and add ammonium molybdate solution and heat to boiling. A canary yellow precipitate is formed.                                                                                                                                                                                                                                           |

**1. Test of Sulphate ions [ $\text{SO}_4^{2-}$ ]**

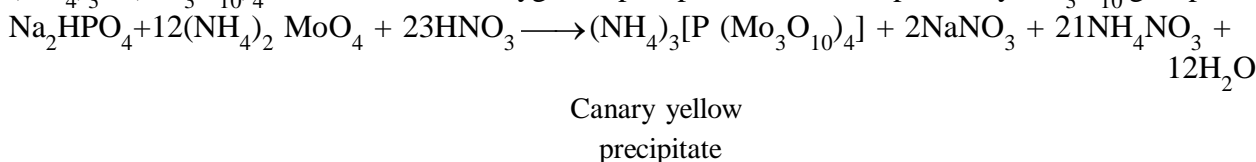
(a) Aqueous solution or sodium carbonate extract of the salt acidified with acetic acid on addition of barium chloride gives a white precipitate of barium sulphate insoluble in conc.  $\text{HCl}$  or conc.  $\text{HNO}_3$ .



(b) Sulphate ions give white precipitate of lead sulphate when aqueous solution or sodium carbonate extract neutralised with acetic acid is treated with lead acetate solution.

**2. Test for Phosphate ion [ $\text{PO}_4^{3-}$ ]**

(a) Add conc.  $\text{HNO}_3$  and ammonium molybdate solution to the test solution containing phosphate ions and boil. A yellow colouration in solution or a canary yellow precipitate of ammonium-phosphomolybdate,  $(\text{NH}_4)_3[\text{P}(\text{Mo}_3\text{O}_{10})_4]$  is formed. Each oxygen of phosphate has been replaced by  $\text{Mo}_3\text{O}_{10}$  group.



## HEATING DEVICES

Heating during the laboratory work can be done with the help of a gas burner, spirit lamp or a kerosene lamp. The gas burner used in the laboratory is usually Bunsen burner . Various parts of Bunsen burner are shown in Fig. The description of these parts is as follows :

### (A) Parts of Bunsen Burner

## 1. The Base

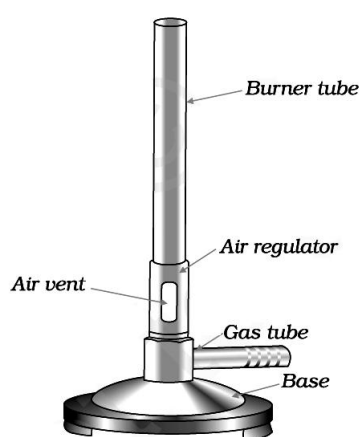
Heavy metallic base is connected to a side tube called gas tube. Gas from the source enters the burner through the gas tube and passes through a small hole called Nipple or Nozzle and enters into the burner tube under increased pressure and can be burnt at the upper end of the burner tube.

## 2. The Burner Tube

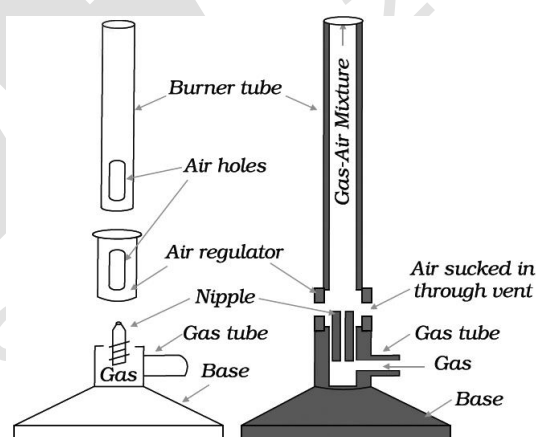
It is a long metallic tube having two holes diametrically opposite to each other near the lower end which form the air vent. The tube can be screwed at the base. The gas coming from the nozzle mixes with the air coming through the air vent and burns at its upper end.

### 3. The Air Regulator

It is a short metallic cylindrical sleeve with two holes diametrically opposite to each other. When it is fitted to the burner tube, it surrounds the air vent of the burner tube. To control the flow of air through the air vent, size of its hole is adjusted by rotating the sleeve.



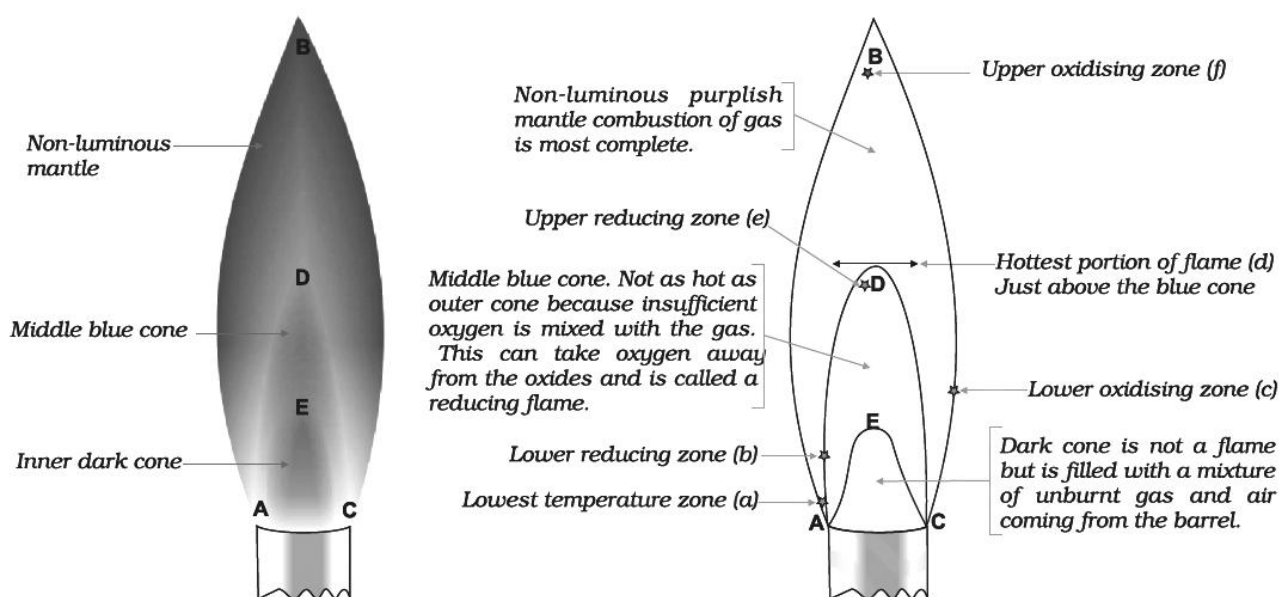
**Fig. Bunsen burner**



**Fig. Parts of Bunsen burner**

If the air vent is closed and the gas is ignited, the flame will be large and luminous (smoky and yellow in colour). The light emitted by the flame is due to the radiations given off by the hot carbon particles of partially burnt fuel. The temperature of the flame in this situation is low. If adjustment of sleeve on vent is such that gas mixed with air is fed into the flame, the flame becomes less luminous and finally turns blue. When the flow of air is correctly adjusted, the temperature of the flame becomes quite high. This is called non-luminous flame. Various zones of flame are shown below in Fig.

Three distinctly visible parts of the Bunsen flame are described below :



**Fig. 1.13 : Zones of flame of Bunsen burner**

## (B) PRINCIPAL PARTS OF BUNSEN FLAME

### 1. The Inner Dark Cone, A E C

This is innermost dark cone, which is just above the burner tube. It consists of unburnt gases. This zone is the coldest zone of the flame and no combustion takes place here.

### 2. The Middle Blue Cone, A D C E A

This is middle part of the flame. This becomes luminous when the air vent is slightly closed. Luminosity of this part is due to the presence of unburnt carbon particles produced by decomposition of some gas. These particles get heated up to incandescence and glow but do not burn. Since the combustion is not complete in this part, the temperature is not very high.

### 3. The Outer Non-luminous Mantle, A B C D A

This is purplish outer cone. It is the hottest part of the flame. It is in direct contact with the atmosphere and combustion is quite complete in this zone.

**Bunsen identified six different regions in these three principal parts of the flame:**

#### (i) The upper oxidising zone (f)

Its location is in the non-luminous tip of the flame which is in the air. In comparison to inner portions of the flame large excess of oxygen is present here. The temperature is not as high as in region (c) described below. It may be used for all oxidation processes in which highest temperature of the flame is not required.

#### (ii) Upper reducing zone (e)

This zone is at the tip of the inner blue cone and is rich in incandescent carbon. It is especially useful for reducing oxide incrustations to the metals.

#### (iii) Hottest portion of flame (d)

It is the fusion zone. It lies at about one-third of the height of the flame and is approximately equidistant from inside and outside of the mantle i.e. the outermost cone of the flame. Fusibility of the substance can be tested in this region. It can also be employed for testing relative volatility of substances or a mixture of substances.

(iv) *Lower oxidising zone (c)*

It is located on the outer border of the mantle near the lower part of the flame and may be used for the oxidation of substances dissolved in beads of borax or sodium carbonate etc.

(v) *Lower reducing zone (b)*

It is situated in the inner edge of the outer mantle near to the blue cone and here reducing gases mix with the oxygen of the air. It is a less powerful reducing zone than (e) and may be employed for the reduction of fused borax and similar beads.

(vi) *Lowest temperature zone (a)*

Zone (a) of the flame has lowest temperature. It is used for testing volatile substances to determine whether they impart colour to the flame.

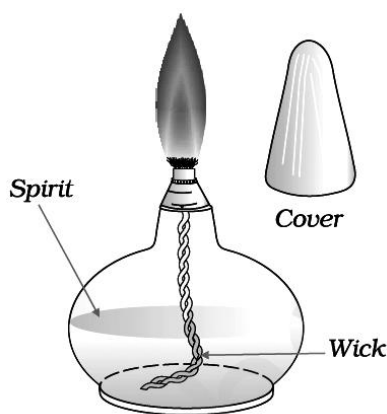
### (C) STRIKING BACK OF THE BUNSEN BURNER

Striking back is the phenomenon in which flame travels down the burner tube and begins to burn at the nozzle near the base. This happens when vents are fully open. The flow of much air and less gas makes the flame become irregular and it strikes back.

The tube becomes very hot and it may produce burns on touching. This may melt attached rubber tube also. If it happens, put off the burner and cool it under the tap and light it again by keeping the air vent partially opened.

### SPIRIT LAMP

If Bunsen burner is not available in the laboratory then spirit lamp can be used for heating. It is a device in which one end of a wick of cotton thread is dipped in a spirit container and the other end of the wick protrudes out of the nozzle at upper end of the container. Spirit rises upto the upper end of the wick due to the capillary action and can be burnt. The flame is non luminous hence can be used for all heating purposes in the laboratory. To put off the lamp, burning wick is covered with the cover. **Never try to put off the lighted burner by blowing at the flame.**



**Fig. 1.14 : The spirit lamp**

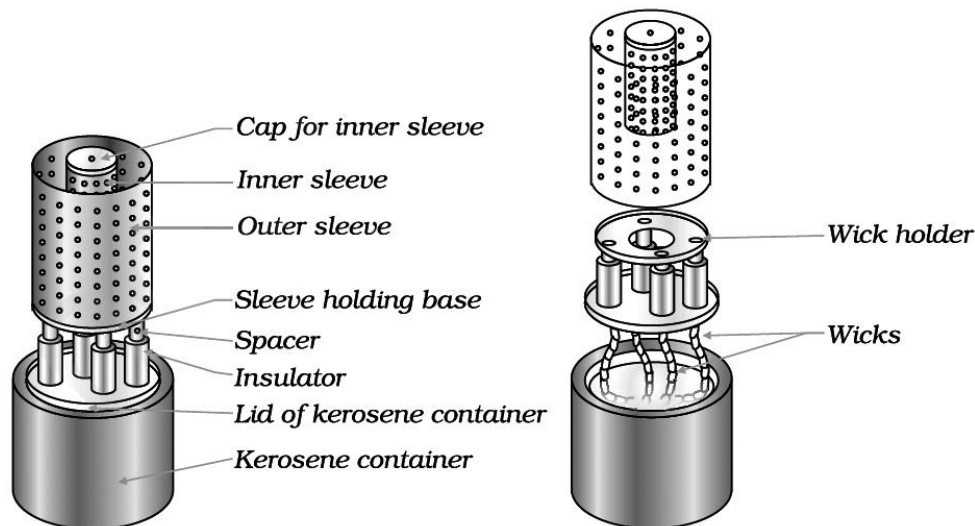
### KEROSENE HEATING LAMP

A kerosene lamp has been developed by National Council of Educational Research and Training (NCERT), which is a versatile and cheaper substitute of spirit lamp. It may be used in laboratories as a source of heat wherever spirit and gas burner are not available. Parts of kerosene lamp are shown in Fig.

#### Working of the Kerosene Lamp

More than half of the container is filled with kerosene. Outer sleeve is removed for lighting the wicks. As the outer sleeve is placed back in position, the flames of four wicks combine to form a big soot-free blue flame.

The lighted heating lamp can be put off only by covering the top of the outer sleeve with a metal or asbestos sheet.



**Fig. 1.15 : Parts of Kerosene Heating Lamp**

## SYSTEMATIC ANALYSIS OF CATIONS

The tests for cations may be carried out according to the following scheme.

### Step - I : Preliminary Examination of the Salt for Identification of Cation

#### 1. Colour Test

Observe the colour of the salt carefully, which may provide useful information about the cations. Table 6 gives the characteristic colours of the salts of some cations.

**Table 6 Characteristic colours of the some metal ions**

| Ion                    | Confirmatory Test |
|------------------------|-------------------|
| Light green            | $\text{Fe}^{2+}$  |
| Yellowish Brown        | $\text{Fe}^{3+}$  |
| Blue                   | $\text{Cu}^{2+}$  |
| Bright green           | $\text{Ni}^{2+}$  |
| Blue, Red Violet, Pink | $\text{Co}^{2+}$  |
| Light pink             | $\text{Mn}^{2+}$  |

#### 2. Dry Heating Test

- Take about 0.1 g of the dry salt in a clean and dry test tube.
- Heat the above test tube for about one minute and observe the colour of the residue when it is hot and also when it becomes cold. Observation of changes gives indications about the presence of cations, which may not be taken as conclusive evidence (see Table 7).

Table 7 : Inferences from the colour of the salt in cold and on heating

| Colour when cold | Colour when hot       | Inference        |
|------------------|-----------------------|------------------|
| Blue             | White                 | $\text{Cu}^{2+}$ |
| Green            | Dirty white or yellow | $\text{Fe}^{2+}$ |
| White            | Yellow                | $\text{Zn}^{2+}$ |
| Pink             | Blue                  | $\text{Co}^{2+}$ |

### 3. Flame Test

The chlorides of several metals impart characteristic colour to the flame because they are volatile in non-luminous flame. This test is performed with the help of a platinum wire as follows :

- Make a tiny loop at one end of a platinum wire.
- To clean the loop dip it into concentrated hydrochloric acid and hold it in a non-luminous flame (Fig. 1.3).
- Repeat step (ii) until the wire imparts no colour to the flame.
- Put 2-3 drops of concentrated hydrochloric acid on a clean watch glass and make a paste of a small quantity of the salt in it.
- Dip the clean loop of the platinum wire in this paste and introduce the loop in the non-luminous (oxidising) flame (Fig. 1.3).
- Observe the colour of the flame first with the naked eye and then through a blue glass and identify the metal ion with the help of Table 8.

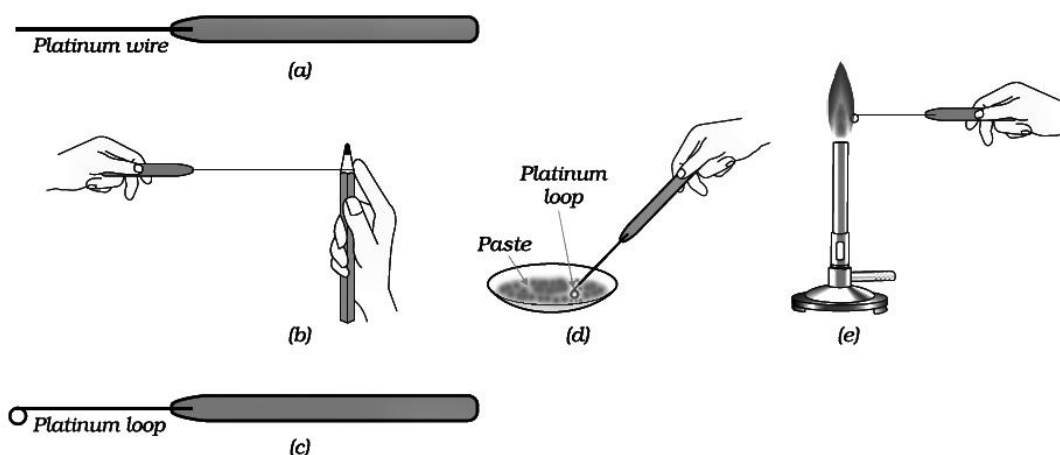


Fig. 1.3 : Performing flame test

Table 8 : Inference from the flame test

| Colour fo the flame observed by naked eye | Colour of the flame observed through blue glass | Inference        |
|-------------------------------------------|-------------------------------------------------|------------------|
| Green flame with blue centre              | Same colour as observed without glass           | $\text{Cu}^{2+}$ |
| Crimson red                               | Purple                                          | $\text{Sr}^{2+}$ |
| Apple green                               | Bluish green                                    | $\text{Ba}^{2+}$ |
| Brick red                                 | Green                                           | $\text{Ca}^{2+}$ |

#### 4. Borax Bead Test

This test is employed only for coloured salts because borax reacts with metal salts to form metal borates or metals, which have characteristic colours.

(i) To perform this test make a loop at the end of the platinum wire and heat it in a flame till it is red hot.

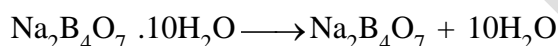
(ii) Dip the hot loop into borax powder and heat it again until borax forms a colourless transparent bead on the loop. Before dipping the borax bead in the test salt or mixture, confirm that the bead is transparent and colourless. If it is coloured this means that, the platinum wire is not clean. Then make a fresh bead after cleaning the wire.

(iii) Dip the bead in a small quantity of the dry salt and again hold it in the flame.

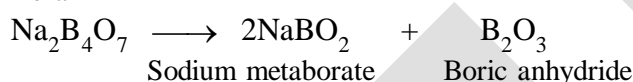
(iv) Observe the colour imparted to the bead in the non-luminous flame as well as in the luminous flame while it is hot and when it is cold (Fig. 1.4).

(v) To remove the bead from the platinum wire, heat it to redness and tap the platinum wire with your finger. (Fig. 1.5).

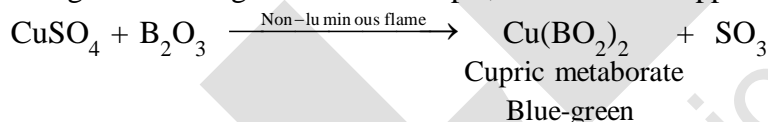
On heating, borax loses its water of crystallisation and decomposes to give sodium metaborate and boric anhydride.



Borax



On treatment with metal salt, boric anhydride forms metaborate of the metal which gives different colours in oxidising and reducing flame. For example, in the case of copper sulphate, following reactions occur.

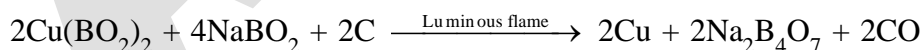


Two reactions may take place in the reducing flame:

(i) The blue  $\text{Cu(BO}_2)_2$  is reduced to colourless cuprous metaborate as follows:



or (ii) Cupric metaborate may be reduced to metallic copper and the bead appears red and opaque.



The preliminary identification of metal ion can be made from Table 9.

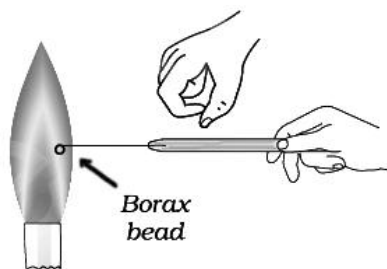


Fig. 1.5 : Removing borax bead

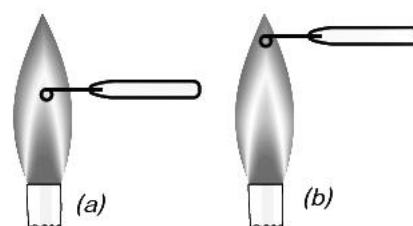


Fig. 1.4 : Borax bead test  
(a) Heating in reducing flame (b) Heating in oxidising flame

Table 9 : Inference from the borax bead test

| Heating in oxidising (non-luminous) flame |                 | Heating in reducing (luminous) flame |            | Inference        |
|-------------------------------------------|-----------------|--------------------------------------|------------|------------------|
| Colour of the salt bead                   |                 | Colour of the salt bead              |            |                  |
| In cold                                   | In hot          | In cold                              | In hot     |                  |
| Blue                                      | Gren            | Red opaque                           | Colourless | Cu <sup>2+</sup> |
| Reddish brown                             | Violet          | Grey                                 | Grey       | Ni <sup>2+</sup> |
| Light violet                              | Light violet    | Colourless                           | Colourless | Mn <sup>2+</sup> |
| Yellow                                    | Yellowish brown | Green                                | Green      | Fe <sup>3+</sup> |

### 5. Charcoal Cavity Test

Metallic carbonate when heated in a charcoal cavity decomposes to give corresponding oxide. The oxide appears as a coloured residue in the cavity. Sometimes oxide may be reduced to metal by the carbon of the charcoal cavity.

The test may be performed as follows:

- Make a small cavity in a charcoal block with the help of a charcoal borer [Fig. 1.6 (a)].
- Fill the cavity with about 0.2 g of the salt and about 0.5 g of anhydrous sodium carbonate.

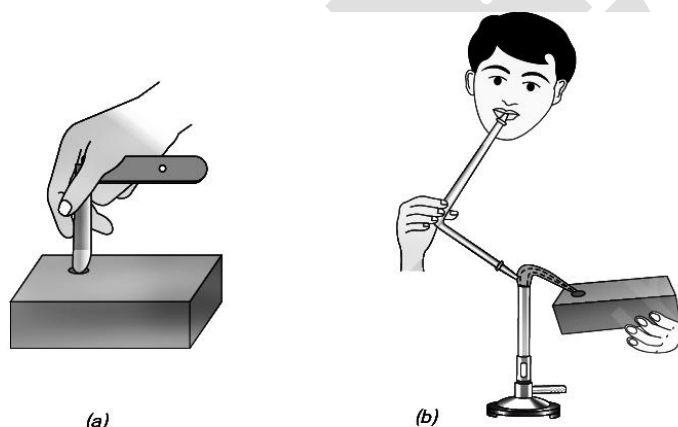


Fig. 1.6 : (a) Making charcoal cavity (b) Heating salt in the cavity

- Moisten the salt in the cavity with one or two drops of water, otherwise salt/mixture will blow away.
- Use a blowpipe to heat the salt in a luminous (reducing) flame and observe the colour of oxide/ metallic bead formed in the cavity both when hot and cold [ Fig. (1.6 b)]. Obtain oxidising and reducing flame as shown in Fig. 1.7 a and b.
- Always bore a fresh cavity for testing the new salt.

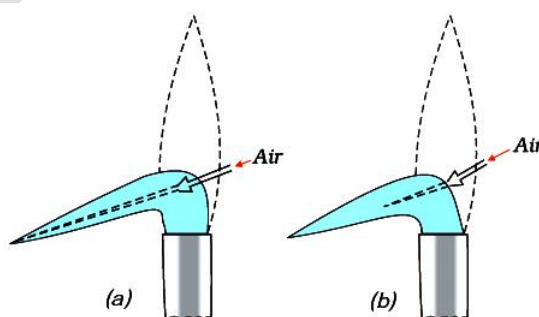
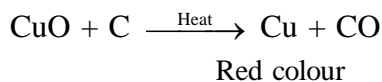
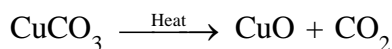
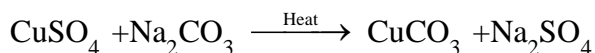


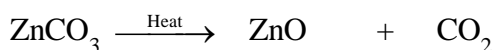
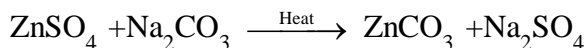
Fig. 1.7 : Obtaining oxidising and reducing flame (a) Oxidising flame; and (b) Reducing flame



When test is performed with  $\text{CuSO}_4$ , the following change occurs.



In case of  $\text{ZnSO}_4$  :



Yellow when hot,

White when cold

The metal ion can be inferred from Table 10.

**Table 10 : Inference from the charcoal cavity test**

| Observations                                     | Inference        |
|--------------------------------------------------|------------------|
| Yellow residue when hot and grey metal when cold | $\text{Pb}^{2+}$ |
| White residue with the odour of garlic           | $\text{As}^{3+}$ |
| Brown residue                                    | $\text{Cd}^{2+}$ |
| Yellow residue when hot and white when cold      | $\text{Zn}^{2+}$ |

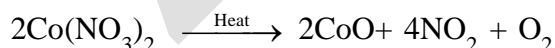
## 6. Cobalt Nitrate Test

If the residue in the charcoal cavity is white, cobalt nitrate test is performed.

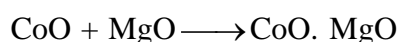
- (i) Treat the residue with two or three drops of cobalt nitrate solution.
- (ii) Heat it strongly in non-luminous flame with the help of a blow pipe and observe the colour of the residue.

On heating, cobalt nitrate decomposes into cobalt (II) oxide, which gives a characteristic colour with metal oxide present in the cavity.

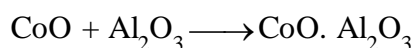
Thus, with  $\text{ZnO}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$ , the following reactions occur.



Green



Pink



Blue

## Step-II : Wet Tests for Identification of Cations

The cations indicated by the preliminary tests given above are confirmed by systematic analysis given below. The first essential step is to prepare a clear and transparent solution of the salt. This is called original solution. It is prepared as follows:

### Preparation of Original Solution (O.S.)

To prepare the original solution, following steps are followed one after the other in a systematic order. In case the salt does not dissolve in a particular solvent even on heating, try the next solvent.

The following solvents are tried:

1. Take a little amount of the salt in a clean boiling tube and add a few mL of distilled water and shake it. If the salt does not dissolved, heat the content of the boiling tube till the salt completely dissolves.
2. If the salt is insoluble in water as detailed above, take fresh salt in a clean boiling tube and add a few mL of dil. HCl to it. If the salt is insoluble in cold, heat the boiling tube till the salt is completely dissolved.
3. If the salt does not dissolve either in water or in dilute HCl even on heating, try to dissolve it in a few mL of conc. HCl by heating.
4. If salt does not dissolve in conc. HCl, then dissolve it in dilute nitric acid.
5. If salt does not dissolve even in nitric acid then a mixture of conc. HCl and conc.  $\text{HNO}_3$  in the ratio 3 : 1 is tried. This mixture is called aqua regia. A salt not soluble in aqua regia is considered to be an insoluble salt.

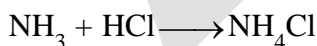
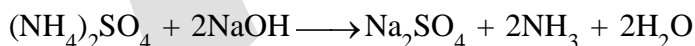
### Group Analysis

#### (I) Analysis of Zero group cation ( $\text{NH}_4^+$ ion)

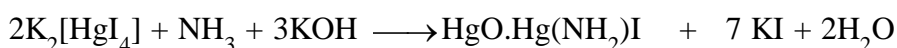
- (a) Take 0.1 g of salt in a test tube and add 1-2 mL of NaOH solution to it and heat. If there is a smell of ammonia, this indicates the presence of ammonium ions. Bring a glass rod dipped in hydrochloric acid near the mouth of the test tube. White fumes are observed.
- (b) Pass the gas through Nessler's reagent. Brown precipitate is obtained.

#### Chemistry of Confirmatory Tests for $\text{NH}_4^+$ ion

- (a) Ammonia gas evolved by the action of sodium hydroxide on ammonium salts reacts with hydrochloric acid to give ammonium chloride, which is visible as dense white fume.



On passing the gas through Nessler's reagent, a brown colouration or a precipitate of basic mercury(II) amido-iodine is formed.



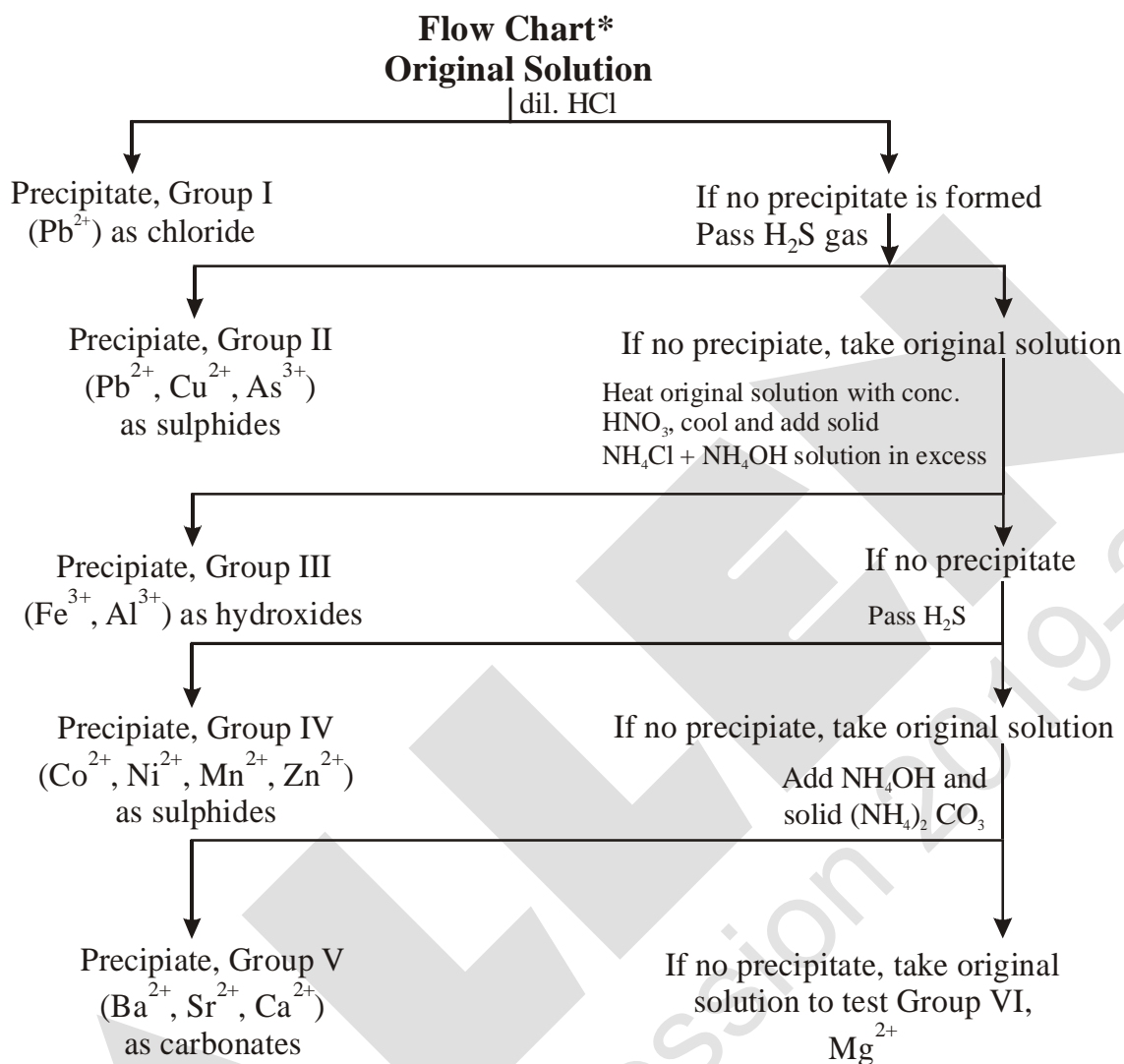
Basic mercury (II)

amido-iodine

(Brown precipitate)

For the analysis of cations belonging to groups I-VI, the cations are precipitated from the original solution by using the group reagents (see Table 1.11) according to the scheme shown in the flow chart given below:

The separation of all the six groups is represented as below :



**Table 11 : Group reagents for precipitating ions**

| Group       | Cations*                                                         | Group Reagent                                                      |
|-------------|------------------------------------------------------------------|--------------------------------------------------------------------|
| Group zero  | $\text{NH}_4^+$                                                  | None                                                               |
| Group - I   | $\text{Pb}^{2+}$                                                 | Dilute HCl                                                         |
| Group - II  | $\text{Pb}^{2+}, \text{Cu}^{2+}, \text{As}^{3+}$                 | $\text{H}_2\text{S}$ gas in presence of dil. HCl                   |
| Group - III | $\text{Al}^{3+}, \text{Fe}^{3+}$                                 | $\text{NH}_4\text{OH}$ in presence of $\text{NH}_4\text{Cl}$       |
| Group - IV  | $\text{Co}^{2+}, \text{Ni}^{2+}, \text{Mn}^{2+}, \text{Zn}^{2+}$ | $\text{H}_2\text{S}$ in presence of $\text{NH}_4\text{OH}$         |
| Group - V   | $\text{Ba}^{2+}, \text{Sr}^{2+}, \text{Ca}^{2+}$                 | $(\text{NH}_4)_2\text{CO}_3$ in presence of $\text{NH}_4\text{OH}$ |
| Group - VI  | $\text{Mg}^{2+}$                                                 | None                                                               |

## (II) Analysis of Group-I cations

Take a small amount of original solution ( if prepared in hot conc. HCl) in a test tube and add cold water to it and cool the test tube under tap water. If a white precipitate appears, this indicates the presence of  $Pb^{2+}$  ions in group –I. On the other hand, if the original solution is prepared in water and on addition of dil. HCl, a white precipitate appears, this may also be  $Pb^{2+}$ . Confirmatory tests are described below in Table 12.

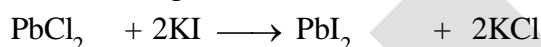
**Table 12 : Confirmatory tests for Group-I cation ( $Pb^{2+}$ )**

| Experiment                                                                                                                                                                                                                                                                                           | Observation                                                                                                                                                                                                                   |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Dissolve the precipitate in hot water and divide the hot solution into three parts,<br>1. Add potassium iodide solution to the first part.<br>2. To the second part add potassium chromate solution.<br>3. To the third part of the hot solution add few drops of alcohol and dilute sulphuric acid. | A yellow precipitate is obtained.<br>A yellow precipitate is obtained which is soluble, in NaOH and insoluble in ammonium acetate solution.<br>A white precipitate is obtained which is soluble in ammonium acetate solution. |

### Chemistry of the Confirmatory Tests of $Pb^{2+}$ ions

Lead is precipitated as lead chloride in the first group. The precipitate is soluble in hot water.

- On adding potassium iodide (KI) solution, a yellow precipitate of lead iodide is obtained which confirms the presence of  $Pb^{2+}$  ions.



(Hot solution) Yellow precipitate

This yellow precipitate ( $PbI_2$ ) is soluble in boiling water and reappears on cooling as shining crystals.

- On addition of potassium chromate ( $K_2CrO_4$ ) solution a yellow precipitate of lead chromate is obtained. This confirms the presence of  $Pb^{2+}$  ions.



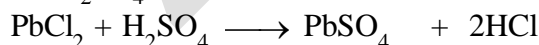
(Hot solution) Lead chromate  
(Yellow precipitate)

The yellow precipitate ( $PbCrO_4$ ) is soluble in hot NaOH solution.



Sodium tetra  
hydroxoplumbate (II)

- A white precipitate of lead sulphate ( $PbSO_4$ ) is formed on addition of alcohol followed by dil.  $H_2SO_4$ .



Lead sulphate  
(White precipitate)

Lead sulphate is soluble in ammonium acetate solution due to the formation of tetraacetatoplumbate(II) ions. This reaction may be promoted by addition of few drops of acetic acid.

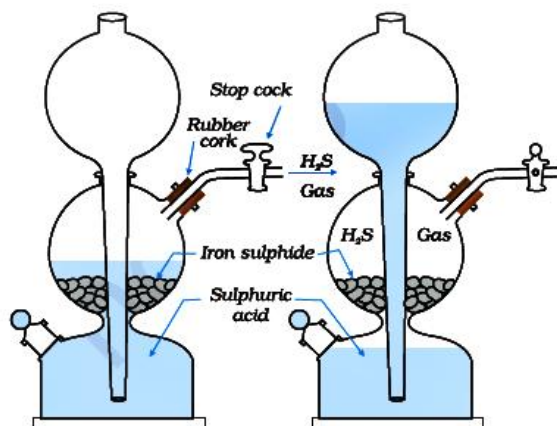


Ammonium  
tetraacetatoplumbate(II)

**(III) Analysis of Group-II cations**

If group-I is absent, add excess of water to the same test tube. Warm the solution and pass  $\text{H}_2\text{S}$  gas for 1-2 minutes (Fig. 1.6). Shake the test tube. If a precipitate appears, this indicates the presence of group-II cations. Pass more  $\text{H}_2\text{S}$  gas through the solution to ensure complete precipitation and separate the precipitate. If the colour of the precipitate is black, it indicates the presence of  $\text{Cu}^{2+}$  or  $\text{Pb}^{2+}$  ions.

If it is yellow in colour, then presence of  $\text{As}^{3+}$  ions is indicated.



**Fig. 1.8 :** Kipp's apparatus for preparation of  $\text{H}_2\text{S}$  gas

Take the precipitate of group-II in a test tube and add excess of yellow ammonium sulphide solution to it. Shake the test tube. If the precipitate is insoluble, group II-A (copper group) is present. If the precipitate is soluble, this indicates the presence of group-II B (arsenic group).

Confirmatory tests for the groups II A and II B are given in Table 13.

**Table 13 : Confirmatory tests for the groups II A and II B cations**

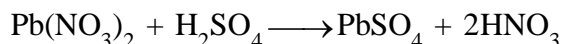
|                                                                                                                                                                                                                                                                                                                                                                                |                                                                                                                                                                                                                    |                                                                                                                                                                                                       |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Black precipitate of Group II A ions $\text{Pb}^{2+}$ , $\text{Cu}^{2+}$ (insoluble in yellow ammonium sulphide) is formed.                                                                                                                                                                                                                                                    |                                                                                                                                                                                                                    | If a yellow precipitate soluble in yellow ammonium sulphide is formed then $\text{As}^{3+}$ ion is present.                                                                                           |
| Boil the precipitate of Group II A with dilute nitric acid and add a few drops of alcohol and dil. $\text{H}_2\text{SO}_4$ .                                                                                                                                                                                                                                                   |                                                                                                                                                                                                                    |                                                                                                                                                                                                       |
| White precipitate confirms the presence of $\text{Pb}^{2+}$ ions. Dissolve the precipitate in ammonium acetate solution. Acidify with acetic acid and divide the solution into two parts.<br>(i) To the first part add potassium chromate solution, a yellow precipitate is formed.<br>(ii) To the second part, add potassium iodide solution, a yellow precipitate is formed. | If no precipitate is formed, add excess of ammonium hydroxide solution. A blue solution is obtained, acidify it with acetic acid and add potassium ferrocyanide solution. A chocolate brown precipitate is formed. |                                                                                                                                                                                                       |
|                                                                                                                                                                                                                                                                                                                                                                                |                                                                                                                                                                                                                    | Acidify this solution with dilute HCl. A yellow precipitate is formed. Heat the precipitate with concentrated nitric acid and add ammonium molybdate solution. A canary yellow precipitate is formed. |

## Group-II A (Copper Group)

### Chemistry of confirmatory tests of Group-II A cations

#### 1. Test for Lead ion ( $\text{Pb}^{2+}$ )

Lead sulphide precipitate dissolves in dilute  $\text{HNO}_3$ . On adding dil.  $\text{H}_2\text{SO}_4$  and a few drops of alcohol to this solution a white precipitate of lead sulphate appears. This indicates the presence of lead ions.

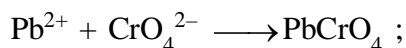


The white precipitate dissolves in ammonium acetate solution on boiling. When this solution is acidified with acetic acid and potassium chromate solution is added, a yellow precipitate of  $\text{PbCrO}_4$  is formed. On adding potassium iodide solution, a yellow precipitate of lead iodide is formed.



Ammonium

tetraacetatoplumbate(II)



Lead chromate

(Yellow precipitate)



Lead iodide

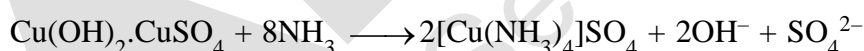
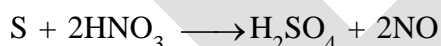
(Yellow precipitate)

#### 2. Test for Copper ion ( $\text{Cu}^{2+}$ )

(a) Copper sulphide dissolves in nitric acid due to the formation of copper nitrate.



On heating the reaction mixture for long time, sulphur is oxidised to sulphate and copper sulphate is formed and the solution turns blue. A small amount of  $\text{NH}_4\text{OH}$  precipitates basic copper sulphate which is soluble in excess of ammonium hydroxide due to the formation of tetraamminecopper (II) complex.

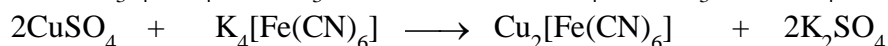
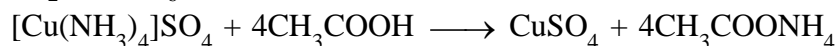


Tetraamminecopper (II)

sulphate (Deep blue)

(b) The blue solution on acidification with acetic acid and then adding potassium ferrocyanide  $\text{K}_4[\text{Fe}(\text{CN})_6]$  solution gives a chocolate colouration due to the formation of copper ferrocyanide

i.e.  $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ .



Potassium

Copper

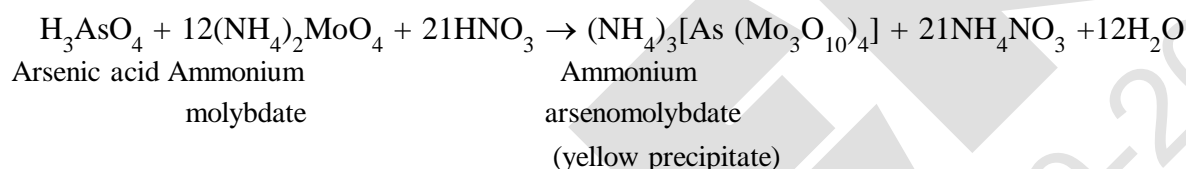
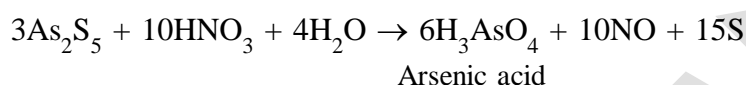
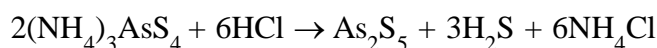
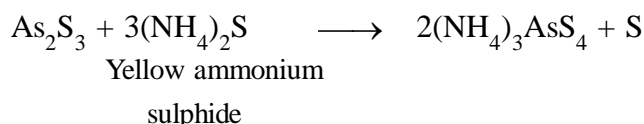
hexacyanoferrate (II)

hexacyanoferrate (II)

(Chocolate brown precipitate)

**Group-II B (Arsenic Group)**

If group-II precipitate dissolves in yellow ammonium sulphide and the colour of the solution is yellow, this indicates the presence of  $\text{As}^{3+}$  ions. Ammonium thioarsenide formed on dissolution of  $\text{As}_2\text{S}_3$ , decomposes with dil.  $\text{HCl}$ , and a yellow precipitate of arsenic (V) sulphide is formed which dissolves in concentrated nitric acid on heating due to the formation of arsenic acid. On adding ammonium molybdate solution to the reaction mixture and heating, a canary yellow precipitate is formed. This confirms the presence of  $\text{As}^{3+}$  ions.

**(IV) Analysis of Group-III cations**

If group-II is absent, take original solution and add 2-3 drops of conc.  $\text{HNO}_3$  to oxidise  $\text{Fe}^{2+}$  ions to  $\text{Fe}^{3+}$  ions. Heat the solution for a few minutes. After cooling add a small amount of solid ammonium chloride ( $\text{NH}_4\text{Cl}$ ) and an excess of ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) solution till it smells of ammonia. Shake the test tube. If a brown or white precipitate is formed, this indicates the presence of group-III cations. Confirmatory tests of group-III cations are summarised in Table 14.

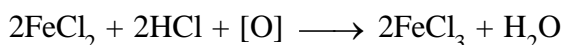
Observe the colour and the nature of the precipitate. A gelatinous white precipitate indicates the presence of aluminium ion ( $\text{Al}^{3+}$ ). If the precipitate is brown in colour, this indicates the presence of ferric ions ( $\text{Fe}^{3+}$ ).

**Table 14 : Confirmatory test for Group-III cations**

|     | <b>Brown precipitate<br/><math>\text{Fe}^{3+}</math></b>                                                                         |     | <b>White precipitate<br/><math>\text{Al}^{3+}</math></b>                                                                                                                                           |
|-----|----------------------------------------------------------------------------------------------------------------------------------|-----|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|     | Dissolve the precipitate in dilute $\text{HCl}$ and divide the solution into two parts.                                          |     | Dissolve the white precipitate in dilute $\text{HCl}$ and divide into two parts.                                                                                                                   |
| (a) | To the first part add potassium ferrocyanide solution [Potassium hexacyanoferrate (II)]. A blue precipitate/colouration appears. | (a) | To the first part add sodium hydroxide solution and warm. A white gelatinous precipitate soluble in excess of sodium hydroxide solution is obtained                                                |
| (b) | To the second part add potassium thiocyanate solution. A blood red colouration appears.                                          | (b) | To the second part first add blue litmus solution and then ammonium hydroxide solution drop by drop along the sides of the test tube. A blue floating mass in the colourless solution is obtained. |

### Chemistry of confirmatory tests of Group - III cations

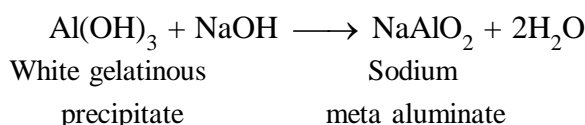
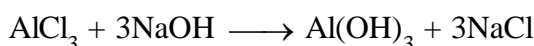
When original solution is heated with concentrated nitric acid, ferrous ion are oxidised to ferric ions.



Their group cations are precipitated as their hydroxides, which dissolve in dilute hydrochloric acid due to the formation of corresponding chlorides.

#### 1. Test for Aluminium ions ( $\text{Al}^{3+}$ )

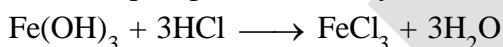
(a) When the solution containing aluminium chloride is treated with sodium hydroxide a white gelatinous precipitate of aluminium hydroxide is formed which is soluble in excess of sodium hydroxide solution due to the formation of sodium meta aluminate.



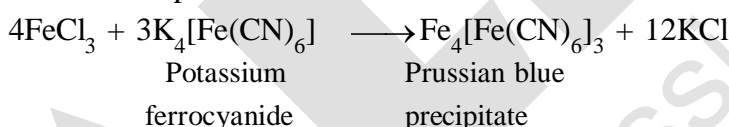
(b) In the second test when blue litmus is added to the solution, a red colouration is obtained due to the acidic nature of the solution. On addition of  $\text{NH}_4\text{OH}$  solution drop by drop, the solution becomes alkaline and aluminium hydroxide is precipitated. Aluminium hydroxide adsorbs blue colour from the solution and forms insoluble adsorption complex named 'lake'. Thus a blue mass floating in the colourless solution is obtained. The test is therefore called **lake test**.

#### 2. Test for ferric ions ( $\text{Fe}^{3+}$ )

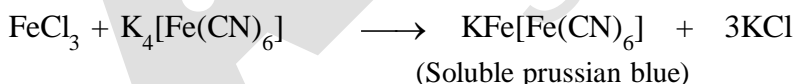
Reddish brown precipitate of ferric hydroxide dissolves in hydrochloric acid and ferric chloride is formed.



(a) When the solution containing ferric chloride is treated with potassium ferrocyanide solution a blue precipitate/colouration is obtained. The colour of the precipitate is Prussian blue. It is ferric ferro-cyanide. The reaction takes place as follows:



If potassium hexacyanoferrate (II) (i.e. potassium ferrocyanide) is added in excess then a product of composition  $\text{KFe}[\text{Fe(CN)}_6]$  is formed. This tends to form a colloidal solution ('soluble Prussian blue') and cannot be filtered.



(b) To the second part of the solution, add potassium thiocyanate (potassium sulphocyanide) solution. The appearance of a blood red colouration confirms the presence of  $\text{Fe}^{3+}$  ions.



#### (V) Analysis of group-IV cations

If group-III is absent, pass  $\text{H}_2\text{S}$  gas in the solution of group-III for a few minutes. If a precipitate appears (white, black or flesh coloured), this indicates the presence of group-IV cations. Table 15 gives a summary of confirmatory tests of group-IV cations.



Table 15 : Confirmatory test for Group - IV cations

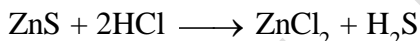
| White precipitate<br>( $\text{Zn}^{2+}$ )                                                                                                                                                                                                                                                                                                                                                                        | Flesh coloured precipitate<br>( $\text{Mn}^{2+}$ )                                                                                                           | Black precipitate<br>( $\text{Ni}^{2+}$ , $\text{Co}^{2+}$ )                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Dissolve the precipitate in dilute HCl by boiling. Divide the solution into two parts.<br>(a) To the first part add sodium hydroxide solution. A white precipitate soluble in excess of sodium hydroxide solution confirms the presence of $\text{Zn}^{2+}$ ions.<br>(b) Neutralise the second part with ammonium hydroxide solution and add potassium ferrocyanide solution. A bluish white precipitate appears | Dissolve the precipitate in dilute HCl by boiling, then add sodium hydroxide solution in excess. A white precipitate is formed which turns brown on keeping. | Dissolve the precipitate in aqua regia. Heat the solution to dryness and cool. Dissolve the residue in water and divide the solution into two parts.<br>(a) To the first part of the solution add ammonium hydroxide solution till it becomes alkaline. Add a few drops of dimethyl glyoxime and shake the test tube. Formation of a bright red precipitate confirms the presence of $\text{Ni}^{2+}$ ions.<br>(b) Neutralise the second part with ammonium hydroxide solution. Acidify it with dilute acetic acid and add solid potassium nitrite. A yellow precipitate confirms the presence of $\text{Co}^{2+}$ ions. |

### Chemistry of confirmatory tests of Group-IV cations

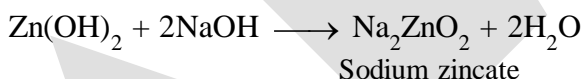
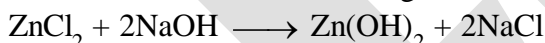
Fourth group cations are precipitated as their sulphides. Observe the colour of the precipitate. A white colour of the precipitate indicates the presence of zinc ions, a flesh colour indicates the presence of manganese ions and a black colour indicates the presence of  $\text{Ni}^{2+}$  or  $\text{Co}^{2+}$  ions.

#### 1. Test for Zinc ion ( $\text{Zn}^{2+}$ )

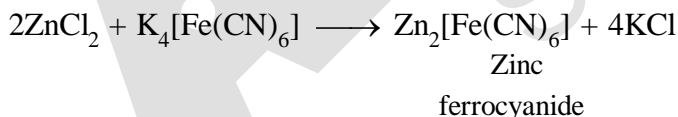
Zinc sulphide dissolves in hydrochloric acid to form zinc chloride.



(a) On addition of sodium hydroxide solution it gives a white precipitate of zinc hydroxide, which is soluble in excess of NaOH solution on heating. This confirms the presence of  $\text{Zn}^{2+}$  ions.

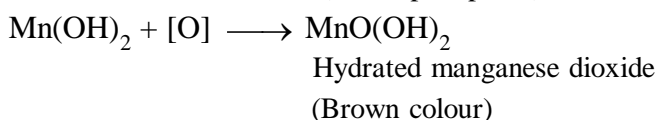
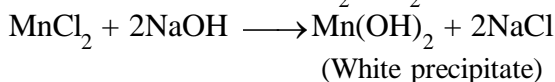
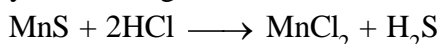


(b) When potassium ferrocyanide  $\text{K}_4[\text{Fe(CN)}_6]$  solution is added to the solution after neutralisation by  $\text{NH}_4\text{OH}$  solution, a white or a bluish white precipitate of zinc ferrocyanide appears.



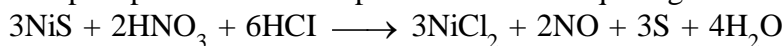
#### 2. Test for Manganese ion ( $\text{Mn}^{2+}$ )

Manganese sulphide precipitate dissolves in dil. HCl on boiling. On addition of NaOH solution in excess, a white precipitate of manganese hydroxide is formed which turns brown due to atmospheric oxidation into hydrated manganese dioxide.

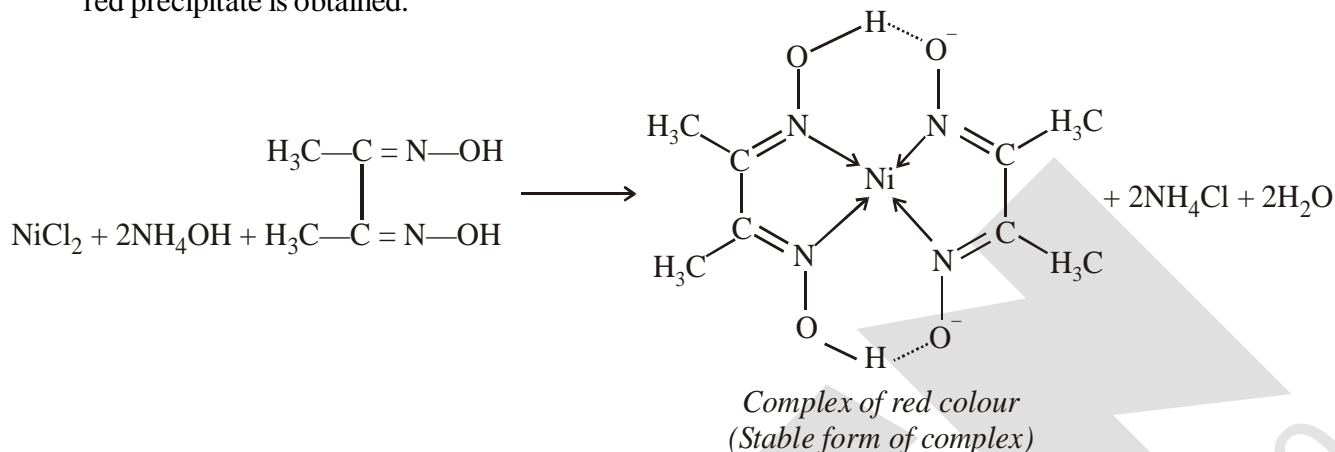


### 3. Test for Nickel ion ( $\text{Ni}^{2+}$ )

The black precipitate of nickel sulphide dissolves in aqua regia and the reaction takes place as follows:

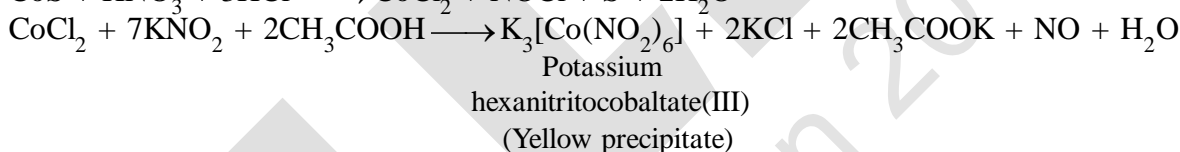
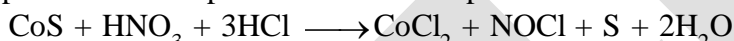


After treatment with aqua regia nickel-chloride is obtained which is soluble in water. When dimethyl glyoxime is added to the aqueous solution of nickel chloride, made alkaline, by adding  $\text{NH}_4\text{OH}$  solution, a brilliant red precipitate is obtained.



### 4. Test for Cobalt ion ( $\text{Co}^{2+}$ )

Cobalt sulphide dissolves in aqua regia in the same manner as nickel sulphide. When the aqueous solution of the residue obtained after treatment with aqua regia is treated with a strong solution of potassium nitrite after neutralisation with ammonium hydroxide and the solution is acidified with dil. acetic acid, a yellow precipitate of the complex of cobalt named potassium hexanitritocobaltate (III) is formed.



### (VI) Analysis of Group-V cations

If group-IV is absent then take original solution and add a small amount of solid  $\text{NH}_4\text{Cl}$  and an excess of  $\text{NH}_4\text{OH}$  solution followed by solid ammonium carbonate  $(\text{NH}_4)_2\text{CO}_3$ . If a white precipitate appears, this indicates the presence of group-V cations.

Dissolve the white precipitate by boiling with dilute acetic acid and divide the solution into three parts one each for  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Ca}^{2+}$  ions. Preserve a small amount of the precipitate for flame test. Summary of confirmatory tests is given in Table 16.

16 : Confirmatory test for Group - V cations

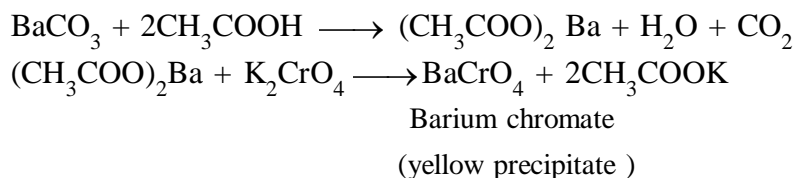
| Dissolve the precipitate by boiling with dilute acetic acid and divide the solution into three parts one each for $\text{Ba}^{2+}$ , $\text{Sr}^{2+}$ and $\text{Ca}^{2+}$ ions                 |                                                                                                                                                                                                                                                                                                                                                             |                                                                                                                                                                                                                                                                                                                                                                                            |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| $\text{Ba}^{2+}$ ions                                                                                                                                                                           | $\text{Sr}^{2+}$ ions                                                                                                                                                                                                                                                                                                                                       | $\text{Ca}^{2+}$ ions                                                                                                                                                                                                                                                                                                                                                                      |
| <p>(a) To the first part add potassium chromate solution. A yellow precipitate appears.</p> <p>(b) Perform the flame test with the preserved precipitate. A grassy green flame is obtained.</p> | <p>(a) If barium is absent, take second part of the solution and add ammonium sulphate solution. Heat and scratch the sides of the test tube with a glass rod and cool. A white precipitate is formed.</p> <p>(b) Perform the flame test with the preserved precipitate. A crimson-red flame confirms the presence of <math>\text{Sr}^{2+}</math> ions.</p> | <p>(a) If both barium and strontium are absent, take the third part of the solution. Add ammonium oxalate solution and shake well. A white precipitate of calcium oxalate is obtained.</p> <p>(b) Perform the flame test with the preserved precipitate. A brick red flame, which looks greenish-yellow through blue glass, confirms the presence of <math>\text{Ca}^{2+}</math> ions.</p> |

**Chemistry of Confirmatory Tests of Group-V cations**

The Group-V cations are precipitated as their carbonates which dissolve in acetic acid due to the formation of corresponding acetates.

**1. Test for Barium ion ( $\text{Ba}^{2+}$ )**

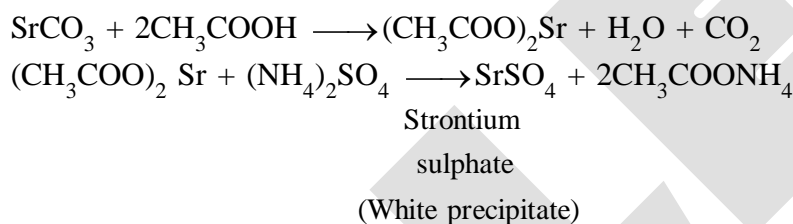
(a) Potassium chromate ( $\text{K}_2\text{CrO}_4$ ) solution gives a yellow precipitate of barium chromate when the solution of fifth group precipitate in acetic acid is treated with it.



(b) **Flame test** : Take a platinum wire and dip it in conc. HCl. Heat it strongly until the wire does not impart any colour to the non-luminous flame. Now dip the wire in the paste of the (Group-V) precipitate in conc. HCl. Heat it in the flame. A grassy green colour of the flame confirms the presence of  $\text{Ba}^{2+}$  ions.

**2. Test for Strontium ion ( $\text{Sr}^{2+}$ )**

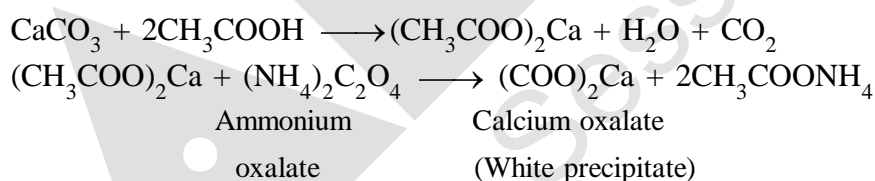
(a) Solution of V group precipitate in acetic acid gives a white precipitate of strontium sulphate with ammonium sulphate solution on heating and scratching the sides of the test tube with a glass rod.



(b) **Flame test** : Perform the flame test as given in the case of  $\text{Ba}^{2+}$ . A crimson red flame confirms the presence of  $\text{Sr}^{2+}$  ions.

**3. Test for Calcium ion ( $\text{Ca}^{2+}$ )**

(a) Solution of the fifth group precipitate in acetic acid gives a white precipitate with ammonium oxalate solution.



(b) **Flame test** : Perform the flame test as mentioned above. Calcium imparts brick red colour to the flame which looks greenish-yellow through blue glass.

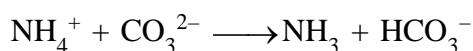
**(VII) Analysis of Group-VI cations**

If group-V is absent then perform the test for  $\text{Mg}^{2+}$  ions as given below.

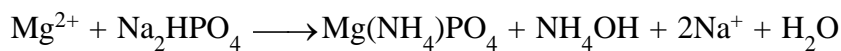
**Chemistry of Confirmatory Tests of Group-VI cations**

Test for Magnesium ion ( $\text{Mg}^{2+}$ )

(a) If group-V is absent then the solution may contain magnesium carbonate, which is soluble in water in the presence of ammonium salts because the equilibrium is shifted towards the right hand side.



The concentration of carbonate ions required to produce a precipitate is not attained. When disodium hydrogenphosphate solution is added and the inner walls of the test tube are scratched with a glass rod, a white crystalline precipitate of magnesium ammonium phosphate is formed which indicates the presence of  $\text{Mg}^{2+}$  ions.



Magnesium ammonium  
phosphate (White precipitate)

Note down the observations and the inferences of the qualitative analysis in tabular form as given in the specimen record

### Precautions



**Fig. 1.9 : How to smell a gas**

- (a) Always use an apron, an eye protector and hand gloves while working in the chemistry laboratory.
- (b) Before using any reagent or a chemical, read the label on the bottle carefully. Never use unlabelled reagent.
- (c) Do not mix chemicals and reagents unnecessarily. Never taste any chemical.
- (d) Be careful in smelling chemicals or vapours.  
Always fan the vapours gently towards your nose (Fig. 1.9).
- (e) Never add sodium metal to water or throw it in the sink or dustbin.
- (f) Always pour acid into water for dilution. Never add water to acid.
- (g) Be careful while heating the test tube. The test tube should never point towards yourself or towards your neighbours while heating or adding a reagent. Fig. 1.9 : How to smell a gas
- (h) Be careful while dealing with the explosive compounds, inflammable substances, poisonous gases, electric appliances, glass wares, flame and the hot substances.

- (i) Keep your working surroundings clean. Never throw papers and glass in the sink. Always use dustbin for this purpose.
- (j) Always wash your hands after the completion of the laboratory work.
- (k) Always use the reagents in minimum quantity. Use of reagents in excess, not only leads to wastage of chemicals but also causes damage to the environment.

### Discussion Questions

- (i) What is the difference between a qualitative and a quantitative analysis?
- (ii) Can we use glass rod instead of platinum wire for performing the flame test? Explain your answer.
- (iii) Why is platinum metal preferred to other metals for the flame test?
- (iv) Name the anions detected with the help of dilute  $\text{H}_2\text{SO}_4$ ?
- (v) Why is dilute  $\text{H}_2\text{SO}_4$  preferred over dilute  $\text{HCl}$  while testing anions?
- (vi) Name the anions detected by conc.  $\text{H}_2\text{SO}_4$ .
- (vii) How is sodium carbonate extract prepared?
- (viii) What is lime water and what happens on passing carbon dioxide gas through it?
- (ix) Carbon dioxide gas and sulphur dioxide gas both turn lime water milky. How will you distinguish these two?
- (x) How will you test the presence of carbonate ion?
- (xi) What is the composition of dark brown ring which is formed at the junction of two layers in the ring test for nitrates?
- (xii) Name the radical confirmed by sodium nitroprusside test.
- (xiii) What is chromyl chloride test? How do you justify that  $\text{CrO}_2\text{Cl}_2$  is acidic in nature?
- (xiv) Why do bromides and iodides not give tests similar to chromyl chloride test?
- (xv) Describe the layer test for bromide and iodide ions.
- (xvi) Why is silver nitrate solution stored in dark coloured bottles?
- (xvii) How do you test the presence of sulphide ion?
- (xviii) Why does iodine give a blue colour with starch solution?
- (xix) What is Nessler's reagent?
- (xx) Why is original solution for cations not prepared in conc.  $\text{HNO}_3$  or  $\text{H}_2\text{SO}_4$ ?
- (xxi) Why cannot conc.  $\text{HCl}$  be used as a group reagent in place of dil.  $\text{HCl}$  for the precipitation of Ist group cations?
- (xxii) How can one prevent the precipitation of Group-IV radicals, with the second group radicals?
- (xxiii) Why is it essential to boil off  $\text{H}_2\text{S}$  gas before precipitation of radicals of group-III?
- (xxiv) Why is heating with conc. nitric acid done before precipitation of group-III?
- (xxv) Can we use ammonium sulphate instead of ammonium chloride in group-III?
- (xxvi) Why is  $\text{NH}_4\text{OH}$  added before  $(\text{NH}_4)_2\text{CO}_3$  solution while precipitating group-V cations?
- (xxvii) Why do we sometimes get a white precipitate in group-VI even if the salt does not contain  $\text{Mg}^{2+}$  radical?
- (xxviii) What is aqua regia?
- (xxix) Name a cation, which is not obtained from a metal.

(xxx) How can you test the presence of ammonium ion?

(xxxi) Why are the group-V radicals tested in the order  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Ca}^{2+}$ ?

(xxxii) Why does conc.  $\text{HNO}_3$  kept in a bottle turn yellow in colour?

(xxxiii) Why should the solution be concentrated before proceeding to group-V?

(xxxiv) Why is the reagent bottle containing sodium hydroxide solution never stoppered?

(xxxv) What do you understand by the term common ion effect?

(xxxvi) Why is zinc sulphide not precipitated in group-II?

### SPECIMEN RECORD OF SALT ANALYSIS

#### Aim

To analyse the given salt for one anion and one cation present in it.

| S. No. | Experiment                                                                                                                                          | Observation                                                                                                            | Inference                                                                                                                                       |
|--------|-----------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------|
| 1.     | Noted the colour of the given salt.                                                                                                                 | White                                                                                                                  | $\text{Cu}^{2+}$ , $\text{Fe}^{2+}$ , $\text{Ni}^{2+}$ , $\text{Co}^{2+}$ , $\text{Mn}^{2+}$ are absent.                                        |
| 2.     | Noted the smell of the salt.                                                                                                                        | No specific smell.                                                                                                     | $\text{S}^{2-}$ , $\text{SO}_3^{2-}$ , $\text{CH}_3\text{COO}^-$ may be absent.                                                                 |
| 3.     | Heated 0.5 g of the salt in a dry test tube and noted the colour of the gas evolved and change in the colour of the residue on heating and cooling. | (i) No gas was evolved.<br>(ii) No particular change in colour of the residue is observed when heated and when cooled. | (i) $\text{CO}_3^{2-}$ may be present, $\text{NO}_3^-$ , $\text{NO}_2^-$ , $\text{Br}^-$ may be absent.<br>(ii) $\text{Zn}^{2+}$ may be absent. |
| 4.     | Prepared a paste of the salt with conc. $\text{HCl}$ and performed the flame test.                                                                  | No distinct colour of the flame seen.                                                                                  | $\text{Ca}^{2+}$ , $\text{Sr}^{2+}$ , $\text{Ba}^{2+}$ , $\text{Cu}^{2+}$ may be absent.                                                        |
| 5.     | Borax bead test was not performed as the salt was white in colour.                                                                                  | —                                                                                                                      | —                                                                                                                                               |
| 6.     | Treated 0.1 g of salt with 1 mL dil. $\text{H}_2\text{SO}_4$ and warmed.                                                                            | No effervescence and evolution of vapours.                                                                             | $\text{CO}_3^{2-}$ , $\text{SO}_3^{2-}$ , $\text{S}^{2-}$ , $\text{NO}_2^-$ , $\text{CH}_3\text{COO}^-$ absent.                                 |
| 7.     | Heated 0.1 g of salt with 1 mL conc. $\text{H}_2\text{SO}_4$ .                                                                                      | No gas evolved.                                                                                                        | $\text{Cl}^-$ , $\text{Br}^-$ , $\text{I}^-$ , $\text{NO}_3^-$ , $\text{C}_2\text{O}_4^{2-}$ are absent.                                        |
| 8.     | Acidified 1 mL of aqueous salt solution with conc. $\text{HNO}_3$ . Warmed the contents and then added 4-5 drops of ammonium molybdate solution.    | No yellow precipitate                                                                                                  | $\text{PO}_4^{3-}$ absent.                                                                                                                      |

| Sl. No. | Experiment                                                                                                                                                                                     | Observation                                                                          | Inference                              |
|---------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|----------------------------------------|
| 9.      | Acidified water extract of the salt with dil. HCl and then added 2mL of BaCl <sub>2</sub> solution.                                                                                            | A white ppt. is obtained which is insoluble in conc. HNO <sub>3</sub> and conc. HCl. | SO <sub>4</sub> <sup>2-</sup> present. |
| 10.     | Heated 0.1 g of salt with 2 mL NaOH solution.                                                                                                                                                  | Ammonia gas is not evolved.                                                          | NH <sub>4</sub> <sup>+</sup> absent.   |
| 11.     | Attempted to prepare original solution of the salt by dissolving 1g of it in 20 mL water.                                                                                                      | Clear solution formed                                                                | Water soluble salt is present.         |
| 12.     | To a small part of the above salt solution added 2 mL of dil. HCl.                                                                                                                             | No white precipitate formed.                                                         | Group-I absent.                        |
| 13.     | Passed H <sub>2</sub> S gas through one portion of the solution of step 12.                                                                                                                    | No precipitate formed.                                                               | Group-II absent.                       |
| 14.     | Since salt is white, heating with conc. HNO <sub>3</sub> is not required. Added about 0.2 g of solid ammonium chloride and then added excess of ammonium hydroxide to the solution of step 12. | No precipitate formed.                                                               | Group-III absent.                      |
| 15.     | Passed H <sub>2</sub> S gas through the above solution.                                                                                                                                        | No precipitate formed.                                                               | Group-IV absent.                       |
| 16.     | Added excess of ammonium hydroxide solution to the original solution and then added 0.5 g of ammonium carbonate.                                                                               | No precipitate formed.                                                               | Group-V absent.                        |
| 17.     | To the original solution of salt added ammonium hydroxide solution, followed by disodium hydrogen phosphate solution. Heated and scratched the sides of the test tube.                         | White precipitate                                                                    | Mg <sup>2+</sup> confirmed.            |

**Result**

**the given salt contains**

**Anion : SO<sub>4</sub><sup>2-</sup>**

**Cation : Mg<sup>2+</sup>**

# EXERCISE # I

## ANIONS : Class A (Subgroup - I)

- The colour developed, when sodium sulphide is added to sodium nitroprusside is:  
(A) Purple (B) yellow (C) red (D) black
- When a neutral or slightly alkaline solution of thiosulphate is treated with the  $[\text{Ni(en)}_3] (\text{NO}_3)_2$  complex, then  
(A) Green precipitate is obtained (B) Brown precipitate is obtained  
(C) Violet precipitate is obtained (D) Yellow precipitate is obtained
- When  $\text{CH}_3\text{COONa}$  heated with solid  $\text{As}_2\text{O}_3$  then compound X is formed. The smell of compound X is -  
(A) Pungent smell (B) Rotten Fish smell (C) Nauseating smell (D) Rotten egg smell
- $\text{NO}_2^-$  ion can be destroyed by -  
(A) Sulphamic acid (B) Thiourea (C) Urea (D) All of these
- Solutions of sodium azide ( $\text{NaN}_3$ ) and iodine (as  $\text{KI}_3$ ) do not react but on addition of a trace of 'X' ion, which acts as a catalyst there is an immediate vigorous evolution of nitrogen. Then 'X' may be:  
(A)  $\text{S}_2\text{O}_3^{2-}$  (B)  $\text{S}^{2-}$  (C)  $\text{SCN}^-$  (D) All are correct.
- When  $\text{AgNO}_3$  react with 'X' ion then initially no visible change occurs due to formation of water soluble complex. Then ion 'X' may be:  
(A)  $\text{SO}_3^{2-}$  (B)  $\text{S}_2\text{O}_3^{2-}$  (C)  $\text{S}^{2-}$  (D)  $\text{CO}_3^{2-}$
- Match the column  

| Column-I                        | Column-II                                                                                       |
|---------------------------------|-------------------------------------------------------------------------------------------------|
| (A) $\text{S}^{2-}$             | (P) Produces white ppt. with excess $\text{AgNO}_3$                                             |
| (B) $\text{HSO}_3^-$            | (Q) Evolves gas with dil. $\text{HCl}$ which turns lime water milky                             |
| (C) $\text{SO}_3^{2-}$          | (R) Evolves gas with dil. $\text{H}_2\text{SO}_4$ which does <b>not</b> turn Baryta water milky |
| (D) $\text{S}_2\text{O}_3^{2-}$ | (S) Produces ppt. with $\text{Pb}(\text{OAc})_2$ solution.                                      |
|                                 | (T) Produces white ppt with $\text{BaCl}_2$ solution.                                           |
- Find the number of acidic radical(s) which can form coloured gas when treated with **dil.**  $\text{H}_2\text{SO}_4$ .  
 $\text{CO}_3^{2-}$ ,  $\text{NO}_2^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{SO}_3^{2-}$

## Class A (Subgroup - II)

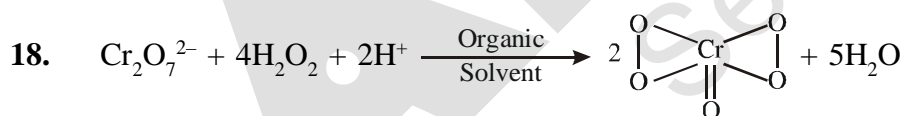
- Chromyl chloride test is given by -  
(A)  $\text{CH}_3\text{Cl}$  (B)  $\text{AgCl}$  (C)  $\text{Hg}_2\text{Cl}_2$  (D)  $\text{NH}_4\text{Cl}$
- $\text{BO}_3^{3-} + \text{H}_2\text{SO}_4 \xrightarrow[\text{Conc.}]{\Delta} \text{(P)}$  White fumes  
 $\text{BO}_3^{3-} + \text{H}_2\text{SO}_4 + \text{C}_2\text{H}_5\text{OH} \xrightarrow[\text{Conc.}]{\Delta} \text{(Q)}$  Vapours  
 P & Q are respectively -  
 (A)  $\text{H}_3\text{BO}_3$ ,  $\text{H}_3\text{BO}_3$  (B)  $(\text{C}_2\text{H}_5)_3\text{BO}_3$ ,  $\text{H}_3\text{BO}_3$   
 (C)  $(\text{C}_2\text{H}_5)_3\text{BO}_3$ ,  $(\text{C}_2\text{H}_5)_3\text{BO}_3$  (D)  $\text{H}_3\text{BO}_3$ ,  $(\text{C}_2\text{H}_5)_3\text{BO}_3$
- In layer test of  $\text{I}^-$  and  $\text{Br}^-$ . If reddish -brown layer comes first then -  
(A)  $\text{Br}^-$  present (B)  $\text{I}^-$  absent (C) Both (A) and (B) (D) None of these



## All Anions Of Class A

12. **Statement-1** : When  $\text{H}_2\text{S}$  gas is passed through Na-nitroprusside solution it gives purple colouration  
**Statement-2** :  $\text{H}_2\text{S}$  is an weak acid  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.
13. When the soda extract containing thiosulphate ion treated with excess of  $\text{AgNO}_3$  solution followed by boiling, then.  
 (A) White precipitate is formed (B) Black precipitate is formed  
 (C) brown precipitate is formed (D) No ppt precipitate is formed
14. "Cacodyl oxide" is formed in the specific test of -  
 (A) Formate (B) Oxalate (C) Acetate (D) Nitrate
15. An aqueous solution of gas (X) gives the white turbidity on passing  $\text{H}_2\text{S}$  in the solution. Identify (X)  
 (A)  $\text{NH}_3$  (B)  $\text{SO}_2$  (C)  $\text{CO}_2$  (D) None of these
16.  $\text{NO}_2^-$  and  $\text{NO}_3^-$  can be distinguished by which of the following reagent.  
 (A) dil.  $\text{H}_2\text{SO}_4$  (B) conc.  $\text{H}_2\text{SO}_4$   
 (C) Devarda's alloy + conc. NaOH (D) None of these
17.  $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$  is unstable because -  
 (A) It liberates NO gas on warming  
 (B) It liberates NO gas on shaking  
 (C) The charge of central atom is +1 (relatively low enough)  
 (D) None of these

## Class B



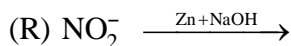
In above reaction amyl alcohol is recommended.

Dimethyl ether is not recommended for general use owing to its -

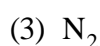
- (A) Highly non-flammable character (B) Highly inflammable character  
 (C) Highly poisonous character (D) None of these
19. If barium sulphate is precipitated in a solution containing potassium permanganate it is coloured pink (violet) by -  
 (A) Absorption of some of the permanganate (B) Adsorption of some of the permanganate  
 (C) Both (A) and (B) (D) None of these

All Anions Of Class A & Class B

20. List-I (Reaction)



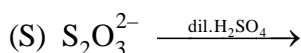
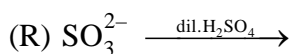
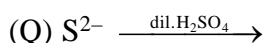
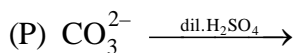
List-II (Product)



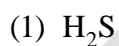
Code :

|     | P | Q | R | S |
|-----|---|---|---|---|
| (A) | 3 | 4 | 1 | 2 |
| (C) | 4 | 2 | 3 | 1 |

21. List-I (Reaction)



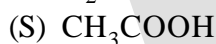
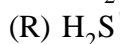
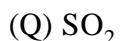
List-II (Product)



Code :

|     | P | Q | R | S |
|-----|---|---|---|---|
| (A) | 3 | 4 | 1 | 2 |
| (C) | 3 | 1 | 2 | 4 |

22. List-I (Molecule)



List-II (Characteristic Odour)

(1) Rotten egg smell

(2) Suffocating smell of burning sulphur

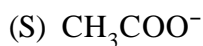
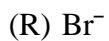
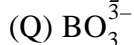
(3) Vinegar like smell

(4) Odour less

Code :

|     | P | Q | R | S |
|-----|---|---|---|---|
| (A) | 4 | 2 | 1 | 3 |
| (C) | 3 | 1 | 2 | 4 |

23. List-I (Acidic radicals)



List-II (Test)

(1) Green flame test

(2) Cacodyl oxide reaction

(3) Griess Ilosvay test

(4) Layer test

Code :

|     | P | Q | R | S |
|-----|---|---|---|---|
| (A) | 4 | 2 | 1 | 3 |
| (C) | 3 | 4 | 2 | 1 |

|     | P | Q | R | S |
|-----|---|---|---|---|
| (B) | 3 | 1 | 4 | 2 |
| (D) | 4 | 3 | 2 | 1 |

## CATIONS : DRY TEST

24. Find the number of water of crystallization in microcosmic salt -  
 (A) 5 (B) 4 (C) 6 (D) 10
25. What is the colour of  $K^+$  through cobalt/double blue glass -  
 (A) Lilac, (B) Violet (C) Brick red (D) Crimson red
26. What is the colour of  $CoO \cdot Al_2O_3$  is -  
 (A) pink (B) Thenard blue (C) Bluish white (D) None of these
27. The correct formula of Canary yellow ppt and it is the test of ----- acid radical-  
 (A)  $(NH_4)_2 [PMo_{12}O_{40}]$  and phosphate (B)  $(NH_4) H [P(Mo_3O_{10})_4]$  and sulphate  
 (C)  $(NH_4)_3 [P(Mo_3O_{10})_4]$  and phosphate (D)  $Na_3 [P(Mo_3O_{10})_4]$  and phosphate
28. Sodium carbonate bead test generally used for .....compounds.  
 (A) Mn (B) Cr (C) Zn (D) Cu

## WET TEST : GROUP ZERO

29. **Statement-1** : Test of  $NH_4^+$  can not be done within group analysis  
**Statement-2** : During group analysis several times  $NH_4^+$  - compound is added at the different steps.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1  
 (C) Statement-1 is false, statement-2 is true.  
 (D) Statement-1 is true, statement-2 is false.

## GROUP - I

30. Which of the following is not group-I cation though the chlorides of all cations are sparingly soluble in water.  
 (A)  $Ag^+$  (B)  $Hg_2^{2+}$  (C)  $Cu^+$  (D)  $Pb^{2+}$

## GROUP - II A

31.  $Cu^{2+} + KCN$  (in excess)  $\rightarrow$  soluble complex (X). How many statements are correct regarding complex (X) -  
 (i) the central atom has the co-ordination number of 6  
 (ii) the central atom has the co-ordination number of 4  
 (iii) the complex is sq.planar  
 (iv) the complex is diamagnetic  
 (v) the complex is paramagnetic
32.  $BiCl_3 \xrightarrow{KI} \text{black ppt (M)} \xrightarrow{\text{excess KI}} \text{soluble complex (N)}$   
 Find the number of moles of  $I^-$  ions involved for the formation of per mole of (N).

## GROUP - II B

33.  $Sn^{2+}$  and  $Sn^{4+}$  can be distinguished by how many of the following methods -  
 (i) by passing  $H_2S$  in their solution (in acidic medium)  
 (ii) by addition of NaOH in their solution  
 (iii) by addition of excess NaOH in their solution  
 (iv) by addition of dil. HCl in their solution  
 (v) by addition of  $HgCl_2$  solution in their solution

GROUP - III

34. What is the group-III reagent is generally used for group analysis.  
 (A)  $\text{NH}_4\text{OH} + \text{NH}_4\text{NO}_3$  (B)  $\text{NH}_4\text{Cl} + (\text{NH}_4)_2\text{CO}_3$   
 (C)  $\text{NH}_4\text{OH} + (\text{NH}_4)_2\text{SO}_4$  (D)  $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$
35.  $\text{CrCl}_3$  solution +  $\text{Na}_2\text{S}$  solution  $\longrightarrow$  ppt(A)  
 The correct formula and colour of A are  
 (A)  $\text{Cr}_2\text{S}_3$ , Black (B)  $\text{Cr}(\text{OH})_3$ , Green  
 (C)  $\text{Na}[\text{Cr}(\text{OH})_4]$ , Green (D) None of these

GROUP - IV

36. The auxiliary reagent in group-IV reagent is  
 (A)  $\text{H}_2\text{S}$  (B)  $\text{dil.HCl}$  (C)  $\text{NaOH}$  (D)  $\text{NH}_4\text{OH}$

All Group Cations

37. Which of the following cation gives ppt in two groups during group analysis.  
 (A)  $\text{Hg}^{2+}$  (B)  $\text{Hg}_2^{2+}$  (C)  $\text{Pb}^{2+}$  (D)  $\text{Cu}^{2+}$
38. Which of the following cation produces coloured ppt with  $\text{Na}_2\text{SO}_4$  solution -  
 (A)  $\text{Pb}^{2+}$  solution (B)  $\text{Ba}^{2+}$  solution (C)  $\text{Hg}^{2+}$  solution (D)  $\text{Ca}^{2+}$  solution
39.  $\text{NH}_4^+$  and  $\text{K}^+$  ions can be distinguished by the use of following reagent  
 (A)  $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$  (B)  $\text{Na}_2[\text{PtCl}_6]$   
 (C)  $\text{HClO}_4$  or  $\text{NaClO}_4$  (D) Boiling with  $\text{NaOH}$
40. Which of the following sulphides is yellow in colour?  
 (A)  $\text{CuS}$  (B)  $\text{CdS}$  (C)  $\text{ZnS}$  (D)  $\text{CoS}$

MISCELLANEOUS

41. List-I (Compound)

- (P)  $\text{HgO}$   
 (Q)  $\text{BaCO}_3$   
 (R)  $\text{Na}_4[\text{Fe}(\text{CN})_5\text{NOS}]$   
 (S)  $\text{KI}_3$

|        |   |   |   |   |
|--------|---|---|---|---|
| Code : | P | Q | R | S |
| (A)    | 3 | 4 | 1 | 2 |
| (C)    | 2 | 4 | 3 | 1 |

List-II (Colour)

- (1) Purple solution  
 (2) Yellow ppt  
 (3) Dark brown  
 (4) White ppt

|     |   |   |   |   |
|-----|---|---|---|---|
|     | P | Q | R | S |
| (B) | 2 | 4 | 1 | 3 |
| (D) | 2 | 4 | 3 | 1 |

42. List-I (Basic Radical)

- (P)  $\text{Al}^{+3}$   
 (Q)  $\text{Zn}^{+2}$   
 (R)  $\text{Ba}^{+2}$   
 (S)  $\text{Pb}^{+2}$

|        |   |   |   |   |
|--------|---|---|---|---|
| Code : | P | Q | R | S |
| (A)    | 4 | 2 | 1 | 3 |
| (C)    | 3 | 1 | 2 | 4 |

List-II (Group)

- (1) II group  
 (2) V group  
 (3) IV group  
 (4) III group

|     |   |   |   |   |
|-----|---|---|---|---|
|     | P | Q | R | S |
| (B) | 2 | 4 | 1 | 3 |
| (D) | 4 | 3 | 2 | 1 |

43. List-I (Cations)

- (P)  $\text{Co}^{+2}$   
 (Q)  $\text{Fe}^{+3}$   
 (R)  $\text{Cu}^{+2}$   
 (S)  $\text{Ca}^{+2}$

|        |   |   |   |   |
|--------|---|---|---|---|
| Code : | P | Q | R | S |
| (A)    | 4 | 2 | 1 | 3 |
| (C)    | 1 | 2 | 3 | 4 |

List-II (Group reagent)

- (1)  $(\text{NH}_4)_2\text{CO}_3$  in presence of  $\text{NH}_4\text{Cl}$   
 (2)  $\text{H}_2\text{S}$  gas in acidic medium  
 (3)  $\text{H}_2\text{S}$  in presence of  $\text{NH}_4\text{OH}$   
 (4)  $\text{NH}_4\text{OH}$  in presence of  $\text{NH}_4\text{Cl}$

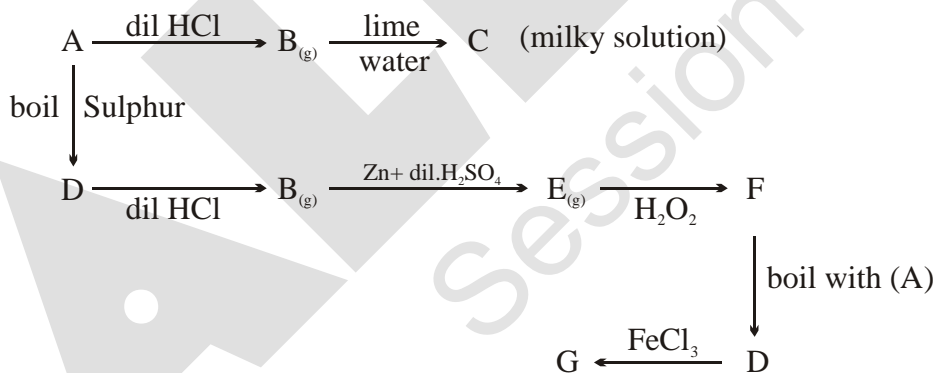
|     |   |   |   |   |
|-----|---|---|---|---|
|     | P | Q | R | S |
| (B) | 3 | 1 | 4 | 2 |
| (D) | 3 | 4 | 2 | 1 |

## EXERCISE # II

## ANIONS : Class A (Subgroup - I)

1. **Statement-1:** On passing  $\text{CO}_2$  gas through lime water, the solution turns milky.  
**because**  
**Statement-2:** Acid-Base (neutralisation) reaction takes place.  
(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
(C) Statement-1 is true, statement-2 is false.  
(D) Statement-1 is false, statement-2 is true.
2. A substance on treatment with dil.  $\text{H}_2\text{SO}_4$  liberates a colourless gas which produces (i) turbidity with baryta water and (ii) turns acidified dichromate solution green. The reaction indicates the presence of  
(A)  $\text{CO}_3^{2-}$  (B)  $\text{S}^{2-}$  (C)  $\text{SO}_3^{2-}$  (D)  $\text{NO}_2^-$
3. When  $\text{S}_2\text{O}_3^{2-}$  react with solution of 'X' reagent then reaction is redox followed by precipitation then 'X' is:  
(A)  $\text{FeCl}_3$  solution (B)  $\text{AgNO}_3$  solution  
(C)  $\text{CuSO}_4$  solution (D) None of these
4. In the test for iodine, when  $\text{I}_2$  is treated with sodium thiosulphate,  $\text{Na}_2\text{S}_2\text{O}_3$   
 $\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 \longrightarrow \text{NaI} + \dots$   
(A)  $\text{Na}_2\text{S}_4\text{O}_6$  (B)  $\text{Na}_2\text{SO}_4$  (C)  $\text{Na}_2\text{S}$  (D)  $\text{Na}_3\text{ISO}_4$

## Paragraph for Q. 5 to Q. 7

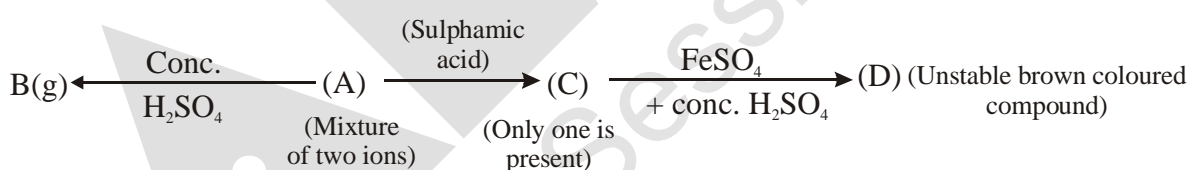


5. Identify A  
(A)  $\text{CO}_3^{2-}$  (B)  $\text{SO}_3^{2-}$  (C)  $\text{S}_2\text{O}_3^{2-}$  (D) none of these
6. When A react with  $\text{Pb}(\text{NO}_3)_2$  then compound X is formed. Compound X is oxidized by atmospheric oxygen on boiling, then Y is formed what is the colour of Y  
(A) yellow (B) White (C) Black (D) Green
7. When gas E react with sodium nitroprusside in basic medium then compound Z is formed. The colour of compound Z is:  
(A) Green (B) purple (C) Reddish brown (D) Black

Class A (Subgroup - II)

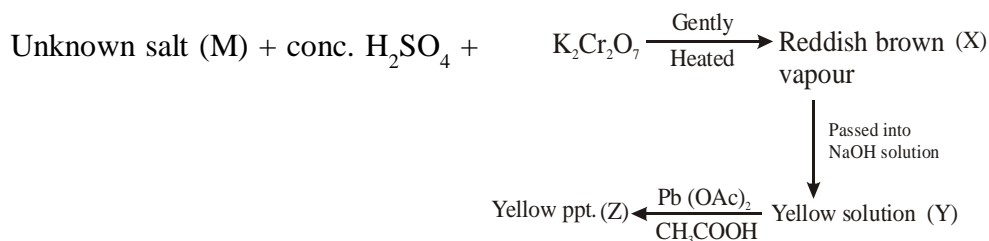
8. When a mixture of solid NaCl, solid  $K_2Cr_2O_7$  is heated with conc.  $H_2SO_4$ , orange red vapours are obtained. These are of the compound  
 (A) chromous chloride (B) chromyl chloride  
 (C) chromic chloride (D) chromic sulphate
9. Which of the following will not give positive chromyl chloride test?  
 (A) Copper chloride,  $CuCl_2$  (B) Mercuric chloride,  $HgCl_2$   
 (C) Zinc chloride,  $ZnCl_2$  (D) Aniline chloride,  $C_6H_5NH_3Cl$
10. Sodium borate on reaction with conc.  $H_2SO_4$  and  $C_2H_5OH$  gives a compound A which burns with a green edged flame. The compound A is  
 (A)  $H_2B_4O_7$  (B)  $(C_2H_5)_2B_4O_7$  (C)  $H_3BO_3$  (D)  $(C_2H_5)_3BO_3$
11. Nitrate is confirmed by ring test. The brown colour of the ring is due to formation of  
 (A) ferrous nitrite (B) nitroso ferrous sulphate  
 (C) ferrous nitrate (D)  $FeSO_4NO_2$
12. A salt gives violet vapours when treated with conc.  $H_2SO_4$ , it contains  
 (A)  $Cl^-$  (B)  $I^-$  (C)  $Br^-$  (D)  $NO_3^-$
13. Unknown salt + Al-powder + NaOH (conc.)  $\rightarrow$  gas comes out which turns Nessler's reagent brown. The salt may be -  
 (A)  $NaNO_2$  (B)  $NaNO_3$  (C)  $NH_4Cl$  (D)  $NH_4HCO_3$

Paragraph for Q. 14 to Q. 17



14. Identify mixture of ions (A) -  
 (A)  $NO_2^-$  and  $Br^-$  (B)  $NO_2^-$  and  $I^-$  (C)  $NO_2^-$  and  $NO_3^-$  (D) None of these
15. What is oxidation state of central atom of (D)  
 (A) +3 (B) +2 (C) +1 (D) Zero
16. Identify gas B-  
 (A)  $Br_2$  (B)  $Br_2 + NO_2$  (C)  $NO_2$  (D) None of these
17. What is the hybridisation of central atom of D-  
 (A)  $d^2sp^3$  (B)  $sp^3d^2$  (C)  $sp^3d$  (D)  $sp^3$

## Paragraph for Q. 18 to Q. 20

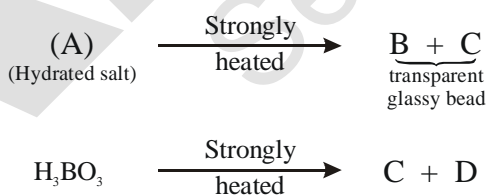


18. The salt (M) is/are-  
 (A) AgCl (B) NH<sub>4</sub>Cl + NaBr (C) NaBr (D) Ca(ClO<sub>4</sub>)<sub>2</sub>
19. How many non axial d-orbitals are involved in hybridisation of central atom of compound (X)-  
 (A) 2 (B) 3 (C) 4 (D) None of these
20. What is the formula of yellow ppt (Z) -  
 (A) BaCrO<sub>4</sub> (B) Na<sub>2</sub>CrO<sub>4</sub> (C) Ag<sub>2</sub>CrO<sub>4</sub> (D) PbCrO<sub>4</sub>

## CATIONS : DRY TEST

21. In the borax bead test of Co<sup>2+</sup>, the blue colour of bead is due to the formation of:  
 (A) B<sub>2</sub>O<sub>3</sub> (B) Co<sub>3</sub>B<sub>2</sub> (C) Co(BO<sub>2</sub>)<sub>2</sub> (D) CoO
22. Which of the following leaves no residue on heating?  
 (A) Pb(NO<sub>3</sub>)<sub>2</sub> (B) NH<sub>4</sub>NO<sub>3</sub> (C) Cu(NO<sub>3</sub>)<sub>2</sub> (D) NaNO<sub>3</sub>
23. Which of the following cations is detected by the flame test?  
 (A) NH<sub>4</sub><sup>+</sup> (B) K<sup>+</sup> (C) Mg<sup>2+</sup> (D) Al<sup>3+</sup>
24. Which metal salt gives a violet coloured bead in the borax bead test (oxidising flame, cold)?  
 (A) Fe<sup>2+</sup> (B) Ni<sup>2+</sup> (C) Co<sup>2+</sup> (D) Mn<sup>2+</sup>
25. The compound formed in the borax bead test of Cu<sup>2+</sup> ion in oxidising flame is:  
 (A) Cu (B) CuBO<sub>2</sub> (C) Cu(BO<sub>2</sub>)<sub>2</sub> (D) None of these
26. In microcosmic salt bead test Co<sup>2+</sup> produce blue bead due to the formation of -  
 (A) Cu(BO<sub>2</sub>)<sub>2</sub> (B) NaCoPO<sub>4</sub> (C) Co<sub>2</sub>(PO<sub>4</sub>)(BO<sub>2</sub>) (D) NaPO<sub>3</sub>

## Paragraph for Q. 27 to Q. 30



27. Identify C-  
 (A) (BN)<sub>x</sub> (B) NaPO<sub>3</sub> (C) B<sub>2</sub>O<sub>3</sub> (D) Mg(NH<sub>4</sub>)PO<sub>4</sub>
28. Find the number of water of crystallizations in (A)-  
 (A) 4 (B) 5 (C) 10 (D) 24
29. How many X-O-X linkages are present in structure of A (X = central atom)-  
 (A) 4 (B) 3 (C) 5 (D) 2
30. Find the number of tetrahedral and trigonal planar units in structure of A -  
 (A) 2,1 (B) 2,2 (C) 2,4 (D) 5,2

### WET TEST : GROUP - I

- 31.** Mercurous ion is represented as:  
(A)  $\text{Hg}_2^{2+}$  (B)  $\text{Hg}^{2+}$  (C)  $\text{Hg} + \text{Hg}^{2+}$  (D)  $\text{Hg}_2^+$
- 32.** A white sodium salt dissolves readily in water to give a solution which is neutral to litmus. When silver nitrate solution is added to the solution, a white precipitate is obtained which does not dissolve in dil.  $\text{HNO}_3$ . The anion could be:  
(A)  $\text{CO}_3^{2-}$  (B)  $\text{Cl}^-$  (C)  $\text{SO}_4^{2-}$  (D)  $\text{S}^{2-}$
- 33.** An aqueous solution of a substance gives a white ppt. on treatment with dil.  $\text{HCl}$ , which dissolves on heating. When hydrogen sulphide is passed through the hot acidic solution, a black ppt. is obtained. The substance is a  
(A)  $\text{Hg}^{2+}$  salt (B)  $\text{Cu}^{2+}$  salt (C)  $\text{Ag}^+$  salt (D)  $\text{Pb}^{2+}$  salt
- 34.** A white ppt obtained in a analysis of a mixture becomes black on treatment with  $\text{NH}_4\text{OH}$ . It may be  
(A)  $\text{PbCl}_2$  (B)  $\text{AgCl}$  (C)  $\text{HgCl}_2$  (D)  $\text{Hg}_2\text{Cl}_2$

## GROUP - II

35. When bismuth chloride is poured into a large volume of water the white precipitate produced is  
(A)  $\text{Bi}(\text{OH})_3$  (B)  $\text{Bi}_2\text{O}_3$  (C)  $\text{BiOCl}$  (D)  $\text{Bi}_2\text{OCl}_3$
36.  $\text{CuSO}_4$  decolourises on addition of excess  $\text{KCN}$ , the product is  
(A)  $[\text{Cu}(\text{CN})_4]^{2-}$ . (B)  $\text{Cu}^{2+}$  get reduced to form  $[\text{Cu}(\text{CN})_4]^{3-}$   
(C)  $\text{Cu}(\text{CN})_2$  (D)  $\text{CuCN}$
37. When  $\text{H}_2\text{S}$  gas is passed through the  $\text{HCl}$  containing aqueous solution of  $\text{CuCl}_2$ ,  $\text{HgCl}_2$ ,  $\text{BiCl}_3$  and  $\text{CoCl}_2$ , it does not precipitate out:  
(A)  $\text{CuS}$  (B)  $\text{HgS}$  (C)  $\text{Bi}_2\text{S}_3$  (D)  $\text{CoS}$
38. Which of the following is soluble in yellow ammonium sulphide?  
(A)  $\text{CuS}$  (B)  $\text{CdS}$  (C)  $\text{SnS}$  (D)  $\text{PbS}$
39. When excess of  $\text{SnCl}_2$  is added to a solution of  $\text{HgCl}_2$ , a white ppt turning grey is obtained. The grey colour is due to the formation of  
(A)  $\text{Hg}_2\text{Cl}_2$  (B)  $\text{SnCl}_4$  (C)  $\text{Sn}$  (D)  $\text{Hg}$
40. On passing  $\text{H}_2\text{S}$  gas in II group sometimes the solution turns milky. It indicates the presence of  
(A) oxidising agent (B) acidic salt (C) s-block cation (D) reducing agent.
41. Which of the following yellow coloured sulphide is insoluble in yellow ammonium sulphide.  
(A)  $\text{SnS}_2$  (B)  $\text{As}_2\text{S}_5$  (C)  $\text{CdS}$  (D)  $\text{Bi}_2\text{S}_3$
42. Type of sulphide ppt may be obtained in the group-II ppt during group analysis.  
(A)  $\text{M}_2\text{S}_3$  (B)  $\text{M}_2\text{S}$  (C)  $\text{MS}$  (D)  $\text{MS}_2$
43. The metal ion which is precipitated when  $\text{H}_2\text{S}$  is passed with  $\text{HCl}$ :  
(A)  $\text{Zn}^{2+}$  (B)  $\text{Ni}^{2+}$  (C)  $\text{Cd}^{2+}$  (D)  $\text{Mn}^{2+}$

### GROUP - III

44. In the precipitation of the iron group in qualitative analysis, ammonium chloride is added before adding ammonium hydroxide to
- (A) decrease concentration of  $\text{OH}^-$  ions.      (B) prevent interference by phosphate ions.
- (C) increase concentration of  $\text{Cl}^-$  ions.      (D) increase concentration of  $\text{NH}_4^+$  ions.



45. If reddish brown ppt (only) is obtained in group-III during group analysis, then oxidation state of Fe in the original sample may be  
 (A) +2 (B) +3 (C) +2 and +3 both (D) Neither +2 nor +3
46. If  $\text{NH}_4\text{Cl}$  is not added to the group-III reagent which of the following ppt could be obtained  
 (A)  $\text{Cr}(\text{OH})_2$  (B)  $\text{Fe}(\text{OH})_3$  (C)  $\text{Mn}(\text{OH})_2$  (D)  $\text{Mg}(\text{OH})_2$
47. In which of the following cases blue ppt is obtained  
 (A)  $\text{Fe}^{2+} + [\text{Fe}(\text{CN})_6]^{3-} \longrightarrow$  (B)  $\text{Fe}^{2+} + [\text{Fe}(\text{CN})_6]^{4-} \longrightarrow$   
 (C)  $\text{Fe}^{3+} + [\text{Fe}(\text{CN})_6]^{4-} \longrightarrow$  (D)  $\text{Fe}^{3+} + [\text{Fe}(\text{CN})_6]^{3-} \xrightarrow{\text{SnCl}_2}$
48. What are the following steps are to be done before adding group-III reagent into the group-II filtrate.  
 (A) Group-II filtrate is to be evaporated to dryness  
 (B) Group-II filtrate is to be boiled of first  
 (C) After boiling 2-3 drops of  $\text{dil. H}_2\text{SO}_4$  is added and boiled again.  
 (D) After boiling 2-3 drops of  $\text{HNO}_3$  is added and boiled again.
49. A pale green crystalline metal salt of M dissolves freely in water. On standing it gives a brown ppt on addition of aqueous NaOH. The metal salt solution also gives a black ppt on bubbling  $\text{H}_2\text{S}$  in basic medium. An aqueous solution of the metal salt decolourizes the pink colour of the permanganate solution. The metal in the metal salt solution is  
 (A) copper (B) aluminium (C) lead (D) iron
50. Which of the following compound on reaction with NaOH and  $\text{Na}_2\text{O}_2$  gives yellow colour?  
 (A)  $\text{Cr}(\text{OH})_3$  (B)  $\text{Zn}(\text{OH})_2$  (C)  $\text{Al}(\text{OH})_3$  (D) None of these

## GROUP - IV

51. Colour of nickel chloride solution is  
 (A) pink (B) black (C) colourless (D) green
52. Dimethyl glyoxime in a suitable solvent was refluxed for 10 minutes with pure pieces of nickel sheet, it will result in  
 (A) Red ppt (B) Blue ppt. (C) Yellow ppt. (D) No ppt.
53. Which one of the following does not produce metallic sulphide with  $\text{H}_2\text{S}$ ?  
 (A)  $\text{ZnCl}_2$  (Neutral sol<sup>n</sup>) (B)  $\text{CdCl}_2$  (aq) (C)  $\text{CoCl}_2$  (aq) (D)  $\text{CuCl}_2$  (aq)
54. Which is not dissolved by dil HCl?  
 (A) ZnS (B) MnS (C)  $\text{BaSO}_3$  (D)  $\text{BaSO}_4$

## GROUP - V

55. In III group,  $\text{NH}_4\text{Cl}$  is added to decrease concentration of hydroxide ion by  $\text{NH}_4\text{OH}$ . We do not add  $(\text{NH}_4)_2\text{SO}_4$  along with  $\text{NH}_4\text{OH}$  because -  
 (A)  $(\text{NH}_4)_2\text{SO}_4$  is insoluble in water (B) It precipitate other insoluble sulphates  
 (C) It is weak electrolyte (D) None of these

## GROUP - VI

56. A metal is burnt in air and the ash on moistening smells of ammonia. The metal is  
 (A) Na (B) Fe (C) Mg (D) Al
57. A metal 'X' on heating in nitrogen gas gives 'Y'. 'Y' on treatment with  $\text{H}_2\text{O}$  gives a colourless gas which when passed through  $\text{CuSO}_4$  solution gives a blue colour Y is:  
 (A)  $\text{Mg}(\text{NO}_3)_2$  (B)  $\text{Mg}_3\text{N}_2$  (C)  $\text{NH}_3$  (D)  $\text{MgO}$

## MISCELLANEOUS

58.  $\text{Na}_2\text{HPO}_4 + \text{Reagent 'M'} \rightarrow \text{white ppt.}$  The reagent 'M' is -  
 (A)  $\text{BaCl}_2$  solution (B)  $\text{AlCl}_3$  solution (C)  $\text{MnSO}_4$  solution (D)  $\text{FeCl}_3$  solution
59. A white solid is first heated with dil  $\text{H}_2\text{SO}_4$  and then with conc.  $\text{H}_2\text{SO}_4$ . No action was observed in either case. The solid salt contains  
 (A) sulphide (B) sulphite (C) thiosulphate (D) sulphate
60. A mixture of chlorides of copper, cadmium, chromium, iron and aluminium was dissolved in water acidified with  $\text{HCl}$  and hydrogen sulphide gas was passed for sufficient time. It was filtered, boiled and a few drops of nitric acid were added while boiling. To this solution ammonium chloride and sodium hydroxide were added in excess and filtered. The filtrate shall give test for  
 (A) sodium and iron ion (B) sodium, chromium and aluminium ion  
 (C) aluminium and iron ion (D) sodium, iron, cadmium and aluminium ion
61. In Nessler's reagent, the ion present is:  
 (A)  $\text{HgI}_2^{2-}$  (B)  $\text{HgI}_4^{2-}$  (C)  $\text{Hg}^+$  (D)  $\text{Hg}^{2+}$
62. The cations present in slightly acidic solution are  $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$ . The reagent which when added in excess to this solution would identify and separate  $\text{Fe}^{3+}$  in one step is:  
 (A) 2 M  $\text{HCl}$  (B) 6 M  $\text{NH}_3$  (C) 6 M  $\text{NaOH}$  (D)  $\text{H}_2\text{S}$  gas
63. In the separation of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  in 2<sup>nd</sup> group qualitative analysis of cation, tetrammine copper (II) sulphate and tetrammine cadmium (II) sulphate react with  $\text{KCN}$  to form the corresponding cyano complexes. Which one of the following pairs of the complexes and their relative stability enables the separation of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$ ?  
 (A)  $\text{K}_3[\text{Cu}(\text{CN})_4]$  more stable and  $\text{K}_2[\text{Cd}(\text{CN})_4]$  less stable.  
 (B)  $\text{K}_2[\text{Cu}(\text{CN})_4]$  less stable and  $\text{K}_2[\text{Cd}(\text{CN})_4]$  more stable.  
 (C)  $\text{K}_2[\text{Cu}(\text{CN})_4]$  more stable and  $\text{K}_2[\text{Cd}(\text{CN})_4]$  less stable.  
 (D)  $\text{K}_3[\text{Cu}(\text{CN})_4]$  less stable and  $\text{K}_2[\text{Cd}(\text{CN})_4]$  more stable.
64. Which one has the minimum solubility product?  
 (A)  $\text{AgCl}$  (B)  $\text{AlCl}_3$  (C)  $\text{BaCl}_2$  (D)  $\text{NH}_4\text{Cl}$
65. Which of the following sulphate is insoluble in water?  
 (A)  $\text{CuSO}_4$  (B)  $\text{CdSO}_4$  (C)  $\text{PbSO}_4$  (D)  $\text{Bi}_2(\text{SO}_4)_3$
66. Which of the following gives blood red colour with  $\text{KSCN}$ ?  
 (A)  $\text{Cu}^{2+}$  (B)  $\text{Fe}^{3+}$  (C)  $\text{Al}^{3+}$  (D)  $\text{Zn}^{2+}$
67. Which one of the following metal sulphide has maximum solubility in water?  
 (A)  $\text{HgS}$ ,  $K_{sp} = 10^{-54}$  (B)  $\text{CdS}$ ,  $K_{sp} = 10^{-30}$   
 (C)  $\text{FeS}$ ,  $K_{sp} = 10^{-20}$  (D)  $\text{ZnS}$ ,  $K_{sp} = 10^{-22}$
68. Identify the correct order of solubility of  $\text{Na}_2\text{S}$ ,  $\text{CuS}$  and  $\text{ZnS}$  in aqueous medium is:  
 (A)  $\text{CuS} > \text{ZnS} > \text{Na}_2\text{S}$  (B)  $\text{ZnS} > \text{Na}_2\text{S} > \text{CuS}$   
 (C)  $\text{Na}_2\text{S} > \text{CuS} > \text{ZnS}$  (D)  $\text{Na}_2\text{S} > \text{ZnS} > \text{CuS}$

69. Match the column -

**Column-I  
(Element)**

- (A) Ba  
(B) Pb  
(C) Ag

(D) Ca

**Column-II****(Correct characteristics)**

- (P) cation in solution produces brick red ppt. with  $\text{CrO}_4^{2-}$   
(Q) cation in solution produces yellow ppt. with  $\text{CrO}_4^{2-}$   
(R) corresponding salt produces apple green colour in the flame test  
(S) corresponding salt produces brick red colour in the flame test  
(T) cation in solution produces no ppt. with  $\text{CrO}_4^{2-}$  ion

70. **Column-I  
Cation in solution**

- (A)  $\text{Ag}^+$  and  $\text{Pb}^{2+}$   
(B)  $\text{Zn}^{2+}$  and  $\text{Mg}^{2+}$   
(C)  $\text{Pb}^{2+}$  and  $\text{Hg}_2^{2+}$   
(D)  $\text{Ag}^+$  and  $\text{Fe}^{3+}$

**Column-I****Correct characteristics when no where excess reagent is used**

- (P) can be distinguished by  $\text{Na}_2\text{HPO}_4$  solution  
(Q) can be distinguished by dil. HCl  
(R) can be distinguished by KI solution  
(S) can not be distinguished by  $\text{NH}_4\text{OH}$  solution

The following column 1, 2, 3 represent the various tests carried out for identification of various group basic radicals, using various reagents and nature of reaction/properties of products observed.

Answer the questions that follow

**Column-1 - Cations/Basic Radical****Column-2 - Excess Reagent used with cation****Column-3 - Nature of Reaction/Properties of product formed**

| Column - 1<br>Cations  | Column - 2<br>Excess Reagent<br>used with cation | Column - 3<br>Nature of Reaction/<br>Properties of product formed |
|------------------------|--------------------------------------------------|-------------------------------------------------------------------|
| (I) $\text{Cu}^{2+}$   | (i) KI (< 6M)                                    | (P) Reduction of cation occurs                                    |
| (II) $\text{Fe}^{3+}$  | (ii) $\text{K}_4[\text{Fe}(\text{CN})_6]$        | (Q) Coloured complex formation                                    |
| (III) $\text{Pb}^{2+}$ | (iii) KCN                                        | (R) Precipitation occurs                                          |
| (IV) $\text{Ni}^{2+}$  | (iv) $\text{NH}_4\text{OH}$                      | (S) Diamagnetic & square planar complex formation                 |

71. For a **group-II** basic radical, which is the only **INCORRECT** combination?  
(A) (I), (i), (P) (B) (IV), (iii), (S) (C) (III), (iv), (R) (D) (III), (iii), (R)
72. For a **group-IV** basic radical, which is the only **CORRECT** combination?  
(A) (I), (iv), (S) (B) (IV), (iii), (P) (C) (II), (iv), (Q) (D) (IV), (iv), (Q)
73. Which combination has a entirely different colour from others?  
(A) (IV), (iv), (Q) (B) (I), (iv), (Q) (C) (II), (iii), (Q) (D) (II), (ii), (Q)
74. How many of the following gives green ppt.  
(i)  $\text{CrCl}_3 + \text{NaOH} \rightarrow$  (ii)  $\text{CrCl}_3 + \text{excess NaOH} \rightarrow$   
(iii)  $\text{NiCl}_2 + \text{excess NaOH} \rightarrow$  (iv)  $\text{NiCl}_2 + \text{excess NH}_4\text{OH} \rightarrow$   
(v)  $\text{Hg}_2^{2+} + \text{KI} \rightarrow$
75. Find the no. of cation which gives white ppt with  $\text{K}_4[\text{Fe}(\text{CN})_6]$   
 $\text{Sr}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$

EXERCISE # JEE MAINS

1. Which products are expected from the disproportionation of hypochlorous acid : [AIEEE-2002]  
 (1)  $\text{HClO}_3$  and  $\text{Cl}_2\text{O}$  (2)  $\text{HClO}_2$  and  $\text{HClO}$  (3)  $\text{HCl}$  and  $\text{Cl}_2\text{O}$  (4)  $\text{HCl}$  and  $\text{HClO}_3$
2. A metal M readily forms its sulphate  $\text{MSO}_4$  which is water soluble. It forms oxide  $\text{MO}$  which becomes inert on heating. It forms insoluble hydroxide which is soluble in  $\text{NaOH}$ . The metal M is:- [AIEEE-2002]  
 (1) Mg (2) Ba (3) Ca (4) Be
3. Which statement is correct :- [AIEEE-2003]  
 (1)  $\text{Fe}^{3+}$  ions give deep green precipitate with  $\text{K}_4[\text{Fe}(\text{CN})_6]$   
 (2) On heating  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  ions, we get a precipitate of  $\text{K}_2[\text{Ca}(\text{CO}_3)_2]$   
 (3) Manganese salts give a violet borax bead test in reducing flame  
 (4) From a mixed precipitate of  $\text{AgCl}$  and  $\text{AgI}$  ammonia solution dissolves only  $\text{AgCl}$
4. What would happen when a solution of potassium chromate is treated with an excess of dilute nitric acid - [AIEEE-2003]  
 (1)  $\text{Cr}^{3+}$  and  $\text{Cr}_2\text{O}_7^{2-}$  are formed (2)  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{H}_2\text{O}$  are formed  
 (3)  $\text{Cr}_2\text{O}_7^{2-}$  is reduced to +3 state of Cr (4)  $\text{Cr}_2\text{O}_7^{2-}$  is oxidised to +7 state of Cr
5. Ammonia forms the complex ion  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  with copper ions in alkaline solutions but not in acidic solution. What is the reason for it :- [AIEEE-2003]  
 (1) In acidic solutions hydration protects copper ions  
 (2) In acidic solutions protons coordinate with ammonia molecules forming  $\text{NH}_4^+$  ions and  $\text{NH}_3$  molecules are not available  
 (3) In alkaline solutions insoluble  $\text{Cu}(\text{OH})_2$  is precipitated which is soluble in excess of any alkali  
 (4) Copper hydroxide is an amphoteric substance
6. Excess of  $\text{KI}$  reacts with  $\text{CuSO}_4$  solution and then  $\text{Na}_2\text{S}_2\text{O}_3$  solution is added to it. Which of the statements is incorrect for this reaction : [AIEEE-2004]  
 (1) Evolved  $\text{I}_2$  is reduced (2)  $\text{CuI}_2$  is formed  
 (3)  $\text{Na}_2\text{S}_2\text{O}_3$  is oxidised (4)  $\text{Cu}_2\text{I}_2$  is formed
7. Calomel on reaction with  $\text{NH}_4\text{OH}$  gives [AIEEE-2004]  
 (1)  $\text{HgNH}_2\text{Cl}$  (2)  $\text{NH}_2\text{-Hg-Hg-Cl}$  (3)  $\text{Hg}_2\text{O}$  (4)  $\text{HgO}$
8. One mole of magnesium nitride on reaction with excess of water gives :- [AIEEE-2004]  
 (1) Two mole of  $\text{HNO}_3$  (2) Two mole of  $\text{NH}_3$   
 (3) 1 mole of  $\text{NH}_3$  (4) 1 mole of  $\text{HNO}_3$
9. The products obtained on heating  $\text{LiNO}_3$  will be :- [AIEEE-2011]  
 (1)  $\text{LiNO}_2 + \text{O}_2$  (2)  $\text{Li}_2\text{O} + \text{NO}_2 + \text{O}_2$   
 (3)  $\text{Li}_3\text{N} + \text{O}_2$  (4)  $\text{Li}_2\text{O} + \text{NO} + \text{O}_2$
10. What is the best description of the change that occurs when  $\text{Na}_2\text{O}(\text{s})$  is dissolved in water ? [AIEEE-2011]  
 (1) Oxidation number of sodium decreases  
 (2) Oxide ion accepts sharing in a pair of electrons  
 (3) Oxide ion donates a pair of electrons  
 (4) Oxidation number of oxygen increases
11. Which of the following on thermal-decomposition yields a basic as well as an acidic oxide ? [AIEEE-2012]  
 (1)  $\text{NH}_4\text{NO}_3$  (2)  $\text{NaNO}_3$  (3)  $\text{KClO}_3$  (4)  $\text{CaCO}_3$
12. The correct statement for the molecule,  $\text{CsI}_3$ , is: [JEE(Main)-2014]  
 (1) it contains  $\text{Cs}^{3+}$  and  $\text{I}^-$  ions (2) it contains  $\text{Cs}^+$ ,  $\text{I}^-$  and lattice  $\text{I}_2$  molecule  
 (3) it is a covalent molecule (4) it contains  $\text{Cs}^+$  and  $\text{I}_3^-$  ions

13. A metal M on heating in nitrogen gas gives Y. Y on treatment with  $\text{H}_2\text{O}$  gives a colourless gas which when passed through  $\text{CuSO}_4$  solution gives a blue colour, Y is :-

[JEE(Main)-2012 online\_P-4]

- (1)  $\text{NH}_3$  (2)  $\text{MgO}$  (3)  $\text{Mg}_3\text{N}_2$  (4)  $\text{Mg}(\text{NO}_3)_2$

14. Potassium dichromate when heated with concentrated sulphuric acid and a soluble chloride, gives brown - red vapours of:

[JEE(Main)-2013 online\_P-1]

- (1)  $\text{CrO}_3$  (2)  $\text{Cr}_2\text{O}_3$  (3)  $\text{CrCl}_3$  (4)  $\text{CrO}_2\text{Cl}_2$

15. Sodium Carbonate cannot be used in place of  $(\text{NH}_4)_2\text{CO}_3$  for the identification of  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$  and  $\text{Sr}^{2+}$  ions (in group V) during mixture analysis because :

[JEE(Main)-2013 online\_P-1]

- (1) Sodium ions will react with acid radicals (2) Concentration of  $\text{CO}_3^{2-}$  ions is very low  
(3)  $\text{Mg}^{2+}$  ions will also be precipitated  
(4)  $\text{Na}^+$  ions will interfere with the detection of  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$  ions

16. Which of the following statements is incorrect?

[JEE(Main)-2013 online\_P-2]

- (1)  $\text{Fe}^{2+}$  ion also gives blood red colour with  $\text{SCN}^-$  ion  
(2) Cupric ion reacts with excess of ammonia solution to give deep blue colour of  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  ion.  
(3)  $\text{Fe}^{3+}$  ion gives blood red colour with  $\text{SCN}^-$  ion.  
(4) On passing  $\text{H}_2\text{S}$  into  $\text{Na}_2\text{ZnO}_2$  solution, a white ppt of  $\text{ZnS}$  is formed.

17. Identify incorrect statement

[JEE(Main)-2013 online\_P-3]

- (1) Copper (I) compounds are colourless except where colour results from charge transfer  
(2) Copper (I) compounds are diamagnetic  
(3)  $\text{Cu}_2\text{S}$  is black (4)  $\text{Cu}_2\text{O}$  is colourless

18. Which one of the following cannot function as an oxidising agent ?

[JEE(Main)-2013 online\_P-4]

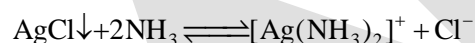
- (1)  $\text{NO}_3^- (\text{aq})$  (2)  $\text{I}^-$  (3)  $\text{Cr}_2\text{O}_7^{2-}$  (4)  $\text{S}_{(\text{s})}$

19. Which of the following statements about  $\text{Na}_2\text{O}_2$  is **not** correct ? [JEE(Main)-2014 online\_P-2]

- (1)  $\text{Na}_2\text{O}_2$  oxidises  $\text{Cr}^{3+}$  to  $\text{CrO}_4^{2-}$  in acid medium (2) It is diamagnetic in nature  
(3) It is the super oxide of sodium (4) It is a derivative of  $\text{H}_2\text{O}_2$

20. Consider the following equilibrium

[JEE(Main)-2014 online\_P-2]

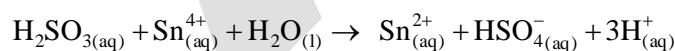


White precipitate of  $\text{AgCl}$  appears on adding which of the following?

- (1)  $\text{NH}_3$  (2) Aqueous  $\text{NaCl}$  (3) Aqueous  $\text{NH}_4\text{Cl}$  (4) Aqueous  $\text{HNO}_3$

21. Consider the reaction

[JEE(Main)-2014 online\_P-4]



Which of the following statements is correct?

- (1)  $\text{H}_2\text{SO}_3$  is the reducing agent because it undergoes oxidation  
(2)  $\text{H}_2\text{SO}_3$  is the reducing agent because it undergoes reduction  
(3)  $\text{Sn}^{4+}$  is the reducing agent because it undergoes oxidation  
(4)  $\text{Sn}^{4+}$  is the oxidizing agent because it undergoes oxidation

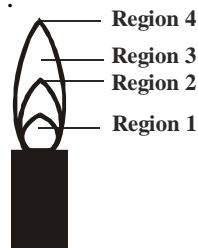
22. Amongst the following, identify the species with an atom in +6 oxidation state :

[JEE(Main)-2014 online\_P-4]

- (1)  $[\text{MnO}_4]^-$  (2)  $[\text{Cr}(\text{CN})_6]^{3-}$  (3)  $\text{Cr}_2\text{O}_3$  (4)  $\text{CrO}_2\text{Cl}_2$

23. The hottest region of Bunsen flame shown in the figure below is : [JEE(Main)-2016]

- (1) region 4
- (2) region 1
- (3) region 2
- (4) region 3



24. Sodium extract is heated with concentrated  $\text{HNO}_3$  before testing for halogens because :

- (1)  $\text{S}^{2-}$  and  $\text{CN}^-$ , if present are decomposed by conc.  $\text{HNO}_3$  and hence do not interfere in the test. [JEE(Main)-2016 online]
- (2) Ag reacts faster with halides in acidic medium
- (3)  $\text{Ag}_2\text{S}$  and  $\text{AgCN}$  are soluble in acidic medium.
- (4) Silver halides are totally insoluble in nitric acid.

25. In the following reactions,  $\text{ZnO}$  is respectively acting as a/an :

- (a)  $\text{ZnO} + \text{Na}_2\text{O} \rightarrow \text{Na}_2\text{ZnO}_2$  (b)  $\text{ZnO} + \text{CO}_2 \rightarrow \text{ZnCO}_3$  [JEE(Main)-2017 off line]
- (1) base and acid (2) base and base (3) acid and acid (4) acid and base

26. The products obtained when chlorine gas reacts with cold and dilute aqueous  $\text{NaOH}$  are :-

- (1)  $\text{ClO}^-$  and  $\text{ClO}_3^-$  (2)  $\text{ClO}_2^-$  and  $\text{ClO}_3^-$  [JEE(Main)-2017 off line]
- (3)  $\text{Cl}^-$  and  $\text{ClO}^-$  (4)  $\text{Cl}^-$  and  $\text{ClO}_2^-$

27. Sodium salt of an organic acid 'X' produces effervescence with conc.  $\text{H}_2\text{SO}_4$ . 'X' reacts with the acidified aqueous  $\text{CaCl}_2$  solution to give a white precipitate which decolourises acidic solution of  $\text{KMnO}_4$ . 'X' is :- [JEE(Main)-2017 off line]

- (1)  $\text{C}_6\text{H}_5\text{COONa}$  (2)  $\text{HCOONa}$  (3)  $\text{CH}_3\text{COONa}$  (4)  $\text{Na}_2\text{C}_2\text{O}_4$

28. A solution containing a group-IV cation gives a precipitate on passing  $\text{H}_2\text{S}$ . A solution of this precipitate in dil.  $\text{HCl}$  produces a white precipitate with  $\text{NaOH}$  solution and bluish-white precipitate with basic potassium ferrocyanide. The cation is : [JEE(Main)-2017 on line]

- (1)  $\text{Mn}^{2+}$  (2)  $\text{Zn}^{2+}$  (3)  $\text{Ni}^{2+}$  (4)  $\text{Co}^{2+}$

29. Which of the following ions does **not** liberate hydrogen gas on reaction with dilute acids?

- (1)  $\text{Ti}^{2+}$  (2)  $\text{Cr}^{2+}$  [JEE(Main)-2017 on line]
- (3)  $\text{Mn}^{2+}$  (4)  $\text{V}^{2+}$

30. When metal 'M' is treated with  $\text{NaOH}$ , a white gelatinous precipitate 'X' is obtained, which is soluble in excess of  $\text{NaOH}$ . Compound 'X' when heated strongly gives an oxide which is used in chromatography as an adsorbent. The metal 'M' is [JEE(Main)-2018 off line]

- (1) Ca (2) Al (3) Fe (4) Zn

31. A white sodium salt dissolves readily in water to give a solution which is neutral to litmus. When silver nitrate solution is added to the aforementioned solution, a white precipitate is obtained which does not dissolve in dil. nitric acid. The anion is : [JEE(Main)-2018 on line]

- (1)  $\text{S}^{2-}$  (2)  $\text{SO}_4^{2-}$  (3)  $\text{CO}_3^{2-}$  (4)  $\text{Cl}^-$

32. The incorrect statement is :- [JEE(Main)-2018 on line]

- (1) Ferric ion gives blood red colour with potassium thiocyanate.
- (2)  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  ions give black precipitate with  $\text{H}_2\text{S}$  in presence of  $\text{HCl}$  solution.
- (3)  $\text{Cu}^{2+}$  salts give red coloured borax bead test in reducing flame.
- (4)  $\text{Cu}^{2+}$  ion gives chocolate coloured precipitate with potassium ferrocyanide solution.

33. When  $\text{XO}_2$  is fused with an alkali metal hydroxide in presence of an oxidizing agent such as  $\text{KNO}_3$ ; a dark green product is formed which disproportionates in acidic solution to afford a dark purple solution. X is : [JEE(Main)-2018 on line]

- (1) Ti (2) Cr (3) V (4) Mn

## EXERCISE # J-ADVANCED

- Which of the following statement(s) is (are) correct with reference to the ferrous and ferric ions:  
 (A)  $\text{Fe}^{3+}$  gives brown colour with potassium ferricyanide [JEE 1998]  
 (B)  $\text{Fe}^{2+}$  gives blue precipitate with potassium ferricyanide  
 (C)  $\text{Fe}^{3+}$  give red colour with potassium thiocyanate  
 (D)  $\text{Fe}^{2+}$  gives brown colour with ammonium thiocyanate
- Which of the following statement(s) is /are correct. When a mixture of  $\text{NaCl}$  and  $\text{K}_2\text{Cr}_2\text{O}_7$  is gently warmed with conc.  $\text{H}_2\text{SO}_4$ ? [JEE 1998]  
 (A) A deep red vapours is evolved.  
 (B) The vapours when passed into  $\text{NaOH}$  solution gives a yellow solution of  $\text{Na}_2\text{CrO}_4$   
 (C) Chlorine gas is evolved  
 (D) Chromyl chloride is formed.
- An aqueous solution of a substance gives a white precipitate on treatment with dilute hydrochloric acid, which dissolves on heating. When hydrogen sulphide is passed through the hot acidic solution, a black precipitate is obtained. The substance is a : [JEE 2000]  
 (A)  $\text{Hg}_2^+$  salt (B)  $\text{Cr}^{2+}$  salt (C)  $\text{Ag}^+$  salt (D)  $\text{Pb}^{2+}$  salt
- A gas 'X' is passed through water to form a saturated solution. The aqueous solution on treatment with silver nitrate gives a white precipitate. The saturated aqueous solution also dissolves magnesium ribbon with evolution of a colourless gas 'Y'. Identify 'X' and 'Y': [JEE 2002(Mains)]  
 (A)  $\text{X} = \text{CO}_2$ ,  $\text{Y} = \text{Cl}_2$  (B)  $\text{X} = \text{Cl}_2$ ,  $\text{Y} = \text{CO}_2$   
 (C)  $\text{X} = \text{Cl}_2$ ,  $\text{Y} = \text{H}_2$  (D)  $\text{X} = \text{H}_2$ ,  $\text{Y} = \text{Cl}_2$
- $[\text{X}] + \text{H}_2\text{SO}_4 \rightarrow [\text{Y}]$  a colourless gas with irritating smell [JEE 2003]  
 $[\text{Y}] + \text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 \longrightarrow$  green solution  
 $[\text{X}]$  and  $[\text{Y}]$  are:  
 (A)  $\text{SO}_3^{2-}$ ,  $\text{SO}_2$  (B)  $\text{Cl}^-$ ,  $\text{HCl}$  (C)  $\text{S}^{2-}$ ,  $\text{H}_2\text{S}$  (D)  $\text{CO}_3^{2-}$ ,  $\text{CO}_2$
- A sodium salt of an unknown anion when treated with  $\text{MgCl}_2$  give white precipitate only on boiling. The anion is: [JEE 2004]  
 (A)  $\text{SO}_4^{2-}$  (B)  $\text{HCO}_3^-$  (C)  $\text{CO}_3^{2-}$  (D)  $\text{NO}_3^-$
- $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  on heating gives a gas which is also given by: [JEE 2004]  
 (A) heating  $\text{NH}_4\text{NO}_2$  (B) heating  $\text{NH}_4\text{NO}_3$   
 (C)  $\text{Mg}_3\text{N}_2 + \text{H}_2\text{O}$  (D)  $\text{NaNO}_2 + \text{H}_2\text{O}_2$

8. A metal nitrate reacts with KI to give a black precipitate which on addition of excess of KI convert into orange colour solution. The cation of metal nitrate is: [JEE 2005]  
 (A)  $\text{Hg}^{2+}$  (B)  $\text{Bi}^{3+}$  (C)  $\text{Pb}^{2+}$  (D)  $\text{Cu}^+$
9. A solution when diluted with  $\text{H}_2\text{O}$  and boiled, it gives a white precipitate. On addition of excess  $\text{NH}_4\text{Cl} / \text{NH}_4\text{OH}$ , the volume of precipitate decreases leaving behind a white gelatinous precipitate. Identify the precipitate which dissolves in  $\text{NH}_4\text{OH} / \text{NH}_4\text{Cl}$ . [JEE 2006]  
 (A)  $\text{Zn}(\text{OH})_2$  (B)  $\text{Al}(\text{OH})_3$  (C)  $\text{Mg}(\text{OH})_2$  (D)  $\text{Ca}(\text{OH})_2$
10.  $\text{CuSO}_4$  decolourises on addition of excess KCN, the product is: [JEE 2006]  
 (A)  $[\text{Cu}(\text{CN})_4]^{2-}$  (B)  $\text{Cu}^{2+}$  get reduced to form  $[\text{Cu}(\text{CN})_4]^{3-}$   
 (C)  $\text{Cu}(\text{CN})_2$  (D)  $\text{CuCN}$
11. Consider a titration of potassium dichromate solution with acidified Mohr's salt solution using diphenylamine as indicator. The number of moles of Mohr's salt required per mole of dichromate is: [JEE 2007]  
 (A) 3 (B) 4 (C) 5 (D) 6
12. The species present in solution when  $\text{CO}_2$  is dissolved in water are [JEE 2007]  
 (A)  $\text{CO}_2, \text{H}_2\text{CO}_3, \text{HCO}_3^-, \text{CO}_3^{2-}$  (B)  $\text{H}_2\text{CO}_3, \text{CO}_3^{2-}$   
 (C)  $\text{CO}_3^{2-}, \text{HCO}_3^-$  (D)  $\text{CO}_2, \text{H}_2\text{CO}_3$
13. Sodium fusion extract, obtained from aniline, on treatment with iron (II) sulphate and  $\text{H}_2\text{SO}_4$  in presence of air gives a Prussian blue precipitate. The blue colour is due to the formation of : [JEE 2007]  
 (A)  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$  (B)  $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$   
 (C)  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_2$  (D)  $\text{Fe}_3[\text{Fe}(\text{CN})_6]_3$
14. **Column I** **Column II** [JEE 2007]  
 (A)  $\text{O}_2^- \rightarrow \text{O}_2 + \text{O}_2^{2-}$  (P) Redox reaction  
 (B)  $\text{CrO}_4^{2-} + \text{H}^+ \rightarrow$  (Q) One of the products has trigonal planar structure  
 (C)  $\text{MnO}_4^- + \text{NO}_2^- + \text{H}^+ \rightarrow$  (R) Dimeric bridged tetrahedral metal ion  
 (D)  $\text{NO}_3^- + \text{H}_2\text{SO}_4 + \text{Fe}^{2+} \rightarrow$  (S) Disproportionation
15. A solution of a metal ion when treated with KI gives a red precipitate which dissolves in excess KI to give a colourless solution. Moreover, the solution of metal ion on treatment with a solution of cobalt (II) thiocyanate gives rise to a deep blue crystalline precipitate. The metal ion is [JEE 2007]  
 (A)  $\text{Pb}^{2+}$  (B)  $\text{Hg}^{2+}$  (C)  $\text{Cu}^{2+}$  (D)  $\text{Co}^{2+}$



16. A solution of colourless salt H on boiling with excess NaOH produces a non-flammable gas. The gas evolution ceases after sometime. Upon addition of Zn dust to the same solution, the gas evolution restarts. The colourless salt(s) H is (are) [JEE 2008]

(A)  $\text{NH}_4\text{NO}_3$  (B)  $\text{NH}_4\text{NO}_2$  (C)  $\text{NH}_4\text{Cl}$  (D)  $(\text{NH}_4)_2\text{SO}_4$

**Paragraph for Question Nos. 17 to 19**

p-Amino-N, N-dimethylaniline is added to a strongly acidic solution of **X**. The resulting solution is treated with a few drops of aqueous solution of **Y** to yield blue coloration due to the formation of methylene blue. Treatment of the aqueous solution of **Y** with the reagent potassium hexacyanoferrate(II) leads to the formation of an intense blue precipitate. The precipitate dissolves on excess addition of the reagent. Similarly, treatment of the solution of **Y** with the solution of potassium hexacyanoferrate(III) leads to a brown coloration due to the formation of **Z**. [JEE 2009]

17. The compound **X** is  
 (A)  $\text{NaNO}_3$  (B)  $\text{NaCl}$  (C)  $\text{Na}_2\text{SO}_4$  (D)  $\text{Na}_2\text{S}$
18. The compound **Y** is  
 (A)  $\text{MgCl}_2$  (B)  $\text{FeCl}_2$  (C)  $\text{FeCl}_3$  (D)  $\text{ZnCl}_2$
19. The compound **Z** is  
 (A)  $\text{Mg}_2[\text{Fe}(\text{CN})_6]$  (B)  $\text{Fe}[\text{Fe}(\text{CN})_6]$  (C)  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$  (D)  $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$
20. Match each of the reactions given in Column I with the corresponding product(s) given in Column II.

**Column I**

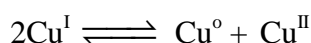
- (A)  $\text{Cu} + \text{dil. HNO}_3$   
 (B)  $\text{Cu} + \text{conc. HNO}_3$   
 (C)  $\text{Zn} + \text{dil. HNO}_3$   
 (D)  $\text{Zn} + \text{conc. HNO}_3$

**Column II**

- (P)  $\text{NO}$   
 (Q)  $\text{NO}_2$   
 (R)  $\text{N}_2\text{O}$   
 (S)  $\text{Cu}(\text{NO}_3)_2$   
 (T)  $\text{Zn}(\text{NO}_3)_2$

[JEE 2009]

21. Passing  $\text{H}_2\text{S}$  gas into a mixture of  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  ions in an acidified aqueous solution precipitates [JEE 2011]  
 (A)  $\text{CuS}$  and  $\text{HgS}$  (B)  $\text{MnS}$  and  $\text{CuS}$  (C)  $\text{MnS}$  and  $\text{NiS}$  (D)  $\text{NiS}$  and  $\text{HgS}$
22. Reduction of the metal centre in aqueous permanganate ion involves - [JEE 2011]  
 (A) 3 electrons in neutral medium (B) 5 electrons in neutral medium  
 (C) 3 electrons in weak alkaline medium (D) 5 electrons in acidic medium
23. The equilibrium [JEE 2011]



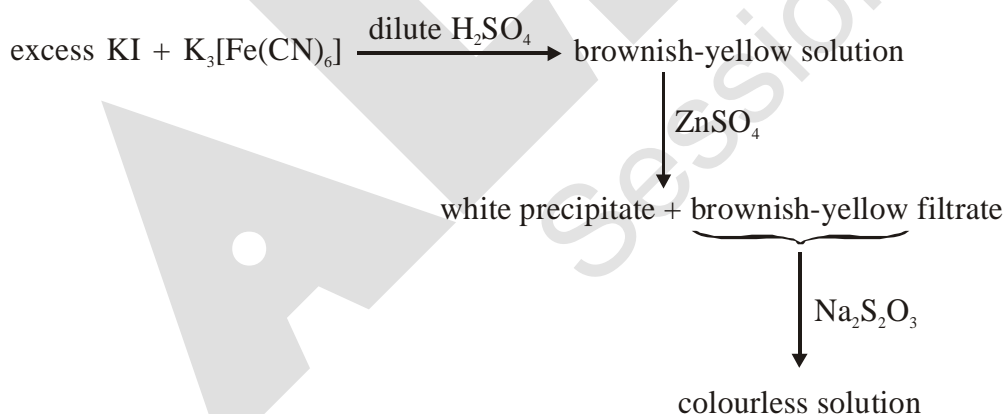
in aqueous medium at  $25^\circ\text{C}$  shifts towards the left in the presence of

(A)  $\text{NO}_3^-$  (B)  $\text{Cl}^-$  (C)  $\text{SCN}^-$  (D)  $\text{CN}^-$

Paragraph for Questions Nos. 24 to 26

When a metal rod M is dipped into an aqueous colourless concentrated solution of compound N, the solution turns light blue. Addition of aqueous NaCl to the blue solution gives a white precipitate O. Addition of aqueous  $\text{NH}_3$  dissolves O and gives an intense blue solution. [JEE 2011]

24. The metal rod M is -  
 (A) Fe (B) Cu (C) Ni (D) Co
25. The compound N is -  
 (A)  $\text{AgNO}_3$  (B)  $\text{Zn(NO}_3)_2$  (C)  $\text{Al(NO}_3)_3$  (D)  $\text{Pb(NO}_3)_2$
26. The final solution contains -  
 (A)  $[\text{Pb(NH}_3)_4]^{2+}$  and  $[\text{CoCl}_4]^{2-}$  (B)  $[\text{Al(NH}_3)_4]^{3+}$  and  $[\text{Cu(NH}_3)_4]^{2+}$   
 (C)  $[\text{Ag(NH}_3)_2]^+$  and  $[\text{Cu(NH}_3)_4]^{2+}$  (D)  $[\text{Ag(NH}_3)_2]^+$  and  $[\text{Ni(NH}_3)_6]^{2+}$
27. Which of the following hydrogen halides react(s) with  $\text{AgNO}_3(\text{aq})$  to give a precipitate that dissolves in  $\text{Na}_2\text{S}_2\text{O}_3(\text{aq})$ : [JEE 2012]  
 (A) HCl (B) HF (C) HBr (D) HI
28. The reaction of white phosphorus with aqueous NaOH gives phosphine along with another phosphorus containing compound. The reaction type ; the oxidation states of phosphorus in phosphine and the other product are respectively [JEE 2012]  
 (A) redox reaction ; -3 and -5 (B) redox reaction ; +3 and +5  
 (C) disproportionation reaction ; -3 and +1 (D) disproportionation reaction ; -3 and +3
29. For the given aqueous reactions, which of the statement(s) is (are) true ? [JEE 2012]



- (A) The first reaction is a redox reaction.  
 (B) White precipitate is  $\text{Zn}_3[\text{Fe(CN)}_6]_2$ .  
 (C) Addition of filtrate to starch solution gives blue colour.  
 (D) White precipitate is soluble in NaOH solution.
30. Upon treatment with ammoniacal  $\text{H}_2\text{S}$ , the metal ion that precipitates as a sulfide is - [JEE 2013]  
 (A) Fe(III) (B) Al(III) (C) Mg(II) (D) Zn (II)

## Paragraph for Question 31 and 32

An aqueous solution of a mixture of two inorganic salts, when treated with dilute HCl, gave a precipitate (**P**) and a filtrate (**Q**). The precipitate (**P**) was found to dissolve in hot water. The filtrate (**Q**) remained unchanged, when treated with  $H_2S$  in a dilute mineral acid medium. However, it gave a precipitate (**R**) with  $H_2S$  in an ammoniacal medium. The precipitate **R** gave a coloured solution (**S**), when treated with  $H_2O_2$  in an aqueous NaOH medium. [JEE 2013]

31. The coloured solution (**S**) contains

- (A)  $Fe_2(SO_4)_3$  (B)  $CuSO_4$  (C)  $ZnSO_4$  (D)  $Na_2CrO_4$

32. The precipitate (**P**) contains

- (A)  $Pb^{2+}$  (B)  $Hg_2^{2+}$  (C)  $Ag^+$  (D)  $Hg^{2+}$

33. Consider the following list of reagents :

[JEE Adv. 2014]

Acidified  $K_2Cr_2O_7$ , alkaline  $KMnO_4$ ,  $CuSO_4$ ,  $H_2O_2$ ,  $Cl_2$ ,  $O_3$ ,  $FeCl_3$ ,  $HNO_3$  and  $Na_2S_2O_3$ .

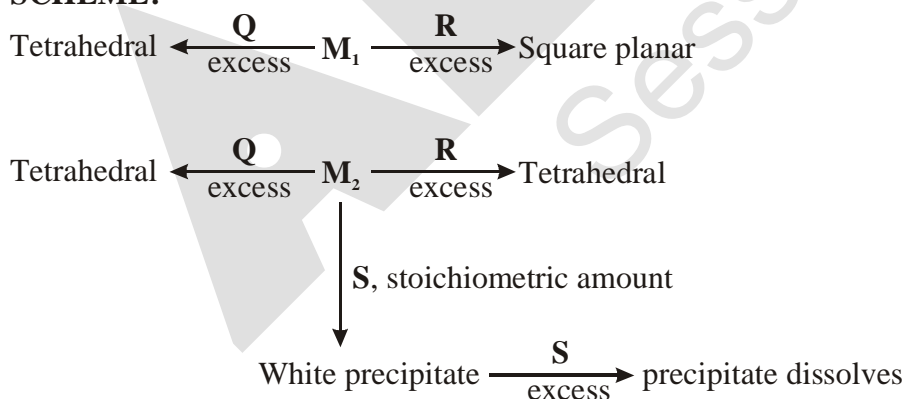
The total number of reagents that can oxidise aqueous iodide to iodine is

34. Among  $PbS$ ,  $CuS$ ,  $HgS$ ,  $MnS$ ,  $Ag_2S$ ,  $NiS$ ,  $CoS$ ,  $Bi_2S_3$ , and  $SnS_2$  the total number of **BLACK** coloured sulphides is [JEE Adv. 2014]

## Paragraph for Q.No. 35 to 36

An aqueous solution of metal ion  $M_1$  reacts separately with reagents **Q** and **R** in excess to give tetrahedral and square planar complexes, respectively. An aqueous solution of another metal ion  $M_2$  always forms tetrahedral complexes with these reagents. Aqueous solution of  $M_2$  on reaction with reagent **S** gives white precipitate which dissolves in excess of **S**. The reactions are summarized in the scheme given below. [JEE Adv. 2014]

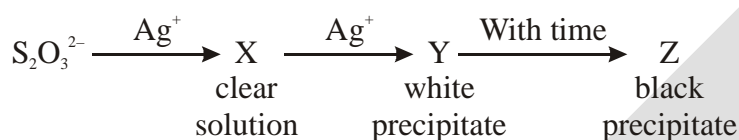
## SCHEME:



35.  $M_1$ , **Q** and **R**, respectively are

- (A)  $Zn^{2+}$ , KCN and HCl (B)  $Ni^{2+}$ , HCl and KCN  
(C)  $Cd^{2+}$ , KCN and HCl (D)  $Co^{2+}$ , HCl and KCN

36. Reagent S is  
 (A)  $K_4[Fe(CN)_6]$  (B)  $Na_2HPO_4$  (C)  $K_2CrO_4$  (D) KOH
37.  $Fe^{3+}$  is reduced to  $Fe^{2+}$  by using - [JEE Adv. 2015]  
 (A)  $H_2O_2$  in presence of NaOH (B)  $Na_2O_2$  in water  
 (C)  $H_2O_2$  in presence of  $H_2SO_4$  (D)  $Na_2O_2$  in presence of  $H_2SO_4$
38. The pair(s) of ions where BOTH the ions are precipitated upon passing  $H_2S$  gas in presence of dilute HCl, is(are) [JEE Adv. 2015]  
 (A)  $Ba^{2+}$ ,  $Zn^{2+}$  (B)  $Bi^{3+}$ ,  $Fe^{3+}$  (C)  $Cu^{2+}$ ,  $Pb^{2+}$  (D)  $Hg^{2+}$ ,  $Bi^{3+}$
39. The reagent(s) that can selectively precipitate  $S^{2-}$  from a mixture of  $S^{2-}$  and  $SO_4^{2-}$  in aqueous solution is(are) : [JEE(Adv.)-2016]  
 (A)  $CuCl_2$  (B)  $BaCl_2$  (C)  $Pb(OOCCH_3)_2$  (D)  $Na_2[Fe(CN)_5NO]$
40. In the following reaction sequence in aqueous solution, the species X, Y and Z respectively, are - [JEE(Adv.)-2016]



- (A)  $[Ag(S_2O_3)_2]^{3-}$ ,  $Ag_2S_2O_3$ ,  $Ag_2S$  (B)  $[Ag(S_2O_3)_3]^{5-}$ ,  $Ag_2SO_3$ ,  $Ag_2S$   
 (C)  $[Ag(SO_3)_2]^{3-}$ ,  $Ag_2S_2O_3$ ,  $Ag$  (D)  $[Ag(SO_3)_3]^{3-}$ ,  $Ag_2SO_4$ ,  $Ag$
41. Which of the following combination will produce  $H_2$  gas ? [JEE(Adv.)-2017]  
 (A) Zn metal and NaOH(aq) (B) Au metal and NaCN(aq) in the presence of air  
 (C) Cu metal and conc.  $HNO_3$  (D) Fe metal and conc.  $HNO_3$
42. Addition of excess aqueous ammonia to a pink coloured aqueous solution of  $MCl_2 \cdot 6H_2O$  (X) and  $NH_4Cl$  gives an octahedral complex Y in the presence of air. In aqueous solution, complex Y behaves as 1 : 3 electrolyte. The reaction of X with excess HCl at room temperature results in the formation of a blue coloured complex Z. The calculated spin only magnetic moment of X and Z is 3.87 B.M., whereas it is zero for complex Y. [JEE(Adv.)-2017]  
 Among the following options, which statements is(are) correct ?  
 (A) The hybridization of the central metal ion in Y is  $d^2sp^3$   
 (B) Z is tetrahedral complex  
 (C) Addition of silver nitrate to Y gives only two equivalents of silver chloride  
 (D) When X and Z are in equilibrium at  $0^\circ C$ , the colour of the solution is pink
43. The correct option(s) to distinguish nitrate salts of  $Mn^{2+}$  and  $Cu^{2+}$  taken separately is (are) :- [JEE(Adv.)-2018]  
 (A)  $Mn^{2+}$  shows the characteristic green colour in the flame test  
 (B) Only  $Cu^{2+}$  shows the formation of precipitate by passing  $H_2S$  in acidic medium  
 (C) Only  $Mn^{2+}$  shows the formation of precipitate by passing  $H_2S$  in faintly basic medium  
 (D)  $Cu^{2+}/Cu$  has higher reduction potential than  $Mn^{2+}/Mn$  (measured under similar conditions)
44. The green colour produced in the borax bead test of a chromium(III) salt is due to- [JEE(Adv.)-2019]  
 (A)  $Cr(BO_2)_3$  (B) CrB (C)  $Cr_2(B_4O_7)_3$  (D)  $Cr_2O_3$

**ANSWER-KEY****EXERCISE # I**

|                                                                                                     |         |           |         |         |           |         |
|-----------------------------------------------------------------------------------------------------|---------|-----------|---------|---------|-----------|---------|
| 1. (A)                                                                                              | 2. (C)  | 3. (C)    | 4. (D)  | 5. (D)  | 6. (A,B)  |         |
| 7. (A) $\rightarrow$ R,S; (B) $\rightarrow$ Q; (C) $\rightarrow$ P,Q,S,T; (D) $\rightarrow$ P,Q,S,T |         |           |         |         | 8. (1)    |         |
| 9. (D)                                                                                              | 10. (D) | 11. (C)   | 12. (D) | 13. (B) | 14. (C)   | 15. (B) |
| 16. (A)                                                                                             | 17. (C) | 18. (B)   | 19. (B) | 20. (D) | 21. (C)   | 22. (A) |
| 23. (B)                                                                                             | 24. (B) | 25. (D)   | 26. (B) | 27. (C) | 28. (A,B) | 29. (A) |
| 30. (C)                                                                                             | 31. (2) | 32. (4)   | 33. (2) | 34. (D) | 35. (B)   | 36. (D) |
| 37. (C)                                                                                             | 38. (C) | 39. (C,D) | 40. (B) | 41. (B) | 42. (D)   | 43. (D) |

**EXERCISE # II**

|                                                                                              |                                                                                           |             |             |             |               |             |
|----------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------|-------------|-------------|-------------|---------------|-------------|
| 1. (B)                                                                                       | 2. (C)                                                                                    | 3. (C)      | 4. (A)      | 5. (B)      | 6. (B)        | 7. (B)      |
| 8. (B)                                                                                       | 9. (B)                                                                                    | 10. (D)     | 11. (B)     | 12. (B)     | 13. (A,B,C,D) | 14. (C)     |
| 15. (C)                                                                                      | 16. (C)                                                                                   | 17. (B)     | 18. (B)     | 19. (B)     | 20. (D)       | 21. (C)     |
| 22. (B)                                                                                      | 23. (B)                                                                                   | 24. (D)     | 25. (C)     | 26. (B)     | 27. (C)       | 28. (C)     |
| 29. (C)                                                                                      | 30. (B)                                                                                   | 31. (A)     | 32. (B)     | 33. (D)     | 34. (D)       | 35. (C)     |
| 36. (B)                                                                                      | 37. (D)                                                                                   | 38. (C)     | 39. (D)     | 40. (A)     | 41. (C)       | 42. (A,C,D) |
| 43. (C)                                                                                      | 44. (A)                                                                                   | 45. (A,B,C) | 46. (B,C,D) | 47. (A,C,D) | 48. (B,D)     | 49. (D)     |
| 50. (A)                                                                                      | 51. (D)                                                                                   | 52. (D)     | 53. (A,C)   | 54. (D)     | 55. (B)       | 56. (C)     |
| 57. (B)                                                                                      | 58. (A,B)                                                                                 | 59. (D)     | 60. (B)     | 61. (B)     | 62. (B)       | 63. (A)     |
| 64. (A)                                                                                      | 65. (C)                                                                                   | 66. (B)     | 67. (C)     | 68. (D)     |               |             |
| 69. (A) $\rightarrow$ Q, R; (B) $\rightarrow$ Q; (C) $\rightarrow$ P; (D) $\rightarrow$ S, T | 70. (A) $\rightarrow$ P; (B) $\rightarrow$ S; (C) $\rightarrow$ R; (D) $\rightarrow$ Q, R |             |             |             |               |             |
| 71. (B)                                                                                      | 72. (D)                                                                                   | 73. (C)     | 74. (3)     | 75. (2)     |               |             |

**EXERCISE # JEE MAINS**

|         |         |         |         |         |         |         |
|---------|---------|---------|---------|---------|---------|---------|
| 1. (4)  | 2. (4)  | 3. (4)  | 4. (2)  | 5. (2)  | 6. (2)  | 7. (1)  |
| 8. (2)  | 9. (2)  | 10. (3) | 11. (4) | 12. (4) | 13. (3) | 14. (4) |
| 15. (3) | 16. (1) | 17. (4) | 18. (2) | 19. (3) | 20. (4) | 21. (1) |
| 22. (4) | 23. (3) | 24. (1) | 25. (4) | 26. (3) | 27. (4) | 28. (2) |
| 29. (3) | 30. (2) | 31. (4) | 32. (2) | 33. (4) |         |         |

**EXERCISE # J-ADVANCED**

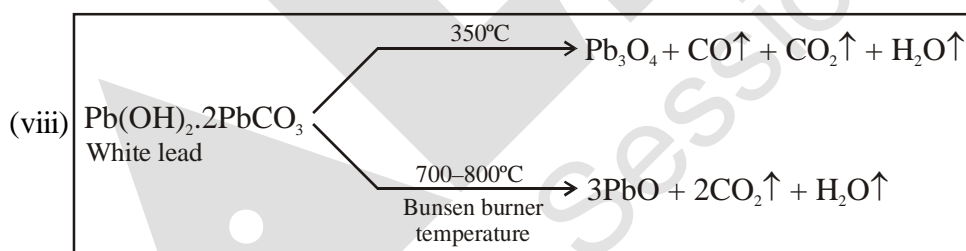
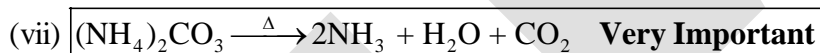
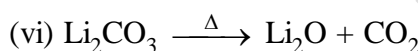
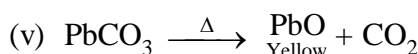
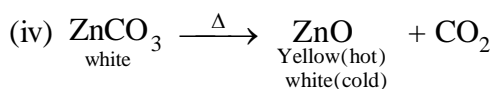
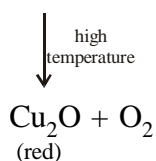
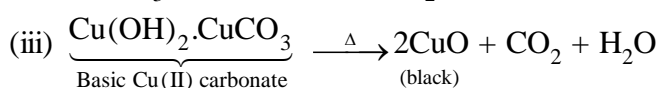
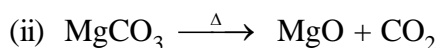
|                                                                                              |              |                                                                                                 |                 |         |               |         |
|----------------------------------------------------------------------------------------------|--------------|-------------------------------------------------------------------------------------------------|-----------------|---------|---------------|---------|
| 1. (A, B, C)                                                                                 | 2. (A, B, D) | 3. (D)                                                                                          | 4. (C)          | 5. (A)  | 6. (B)        | 7. (A)  |
| 8. (B)                                                                                       | 9. (A)       | 10. (B)                                                                                         | 11. (D)         | 12. (A) | 13. (A)       |         |
| 14. (A) $\rightarrow$ P, S; (B) $\rightarrow$ R; (C) $\rightarrow$ P, Q; (D) $\rightarrow$ P | 15. (B)      | 16. (A),(B)                                                                                     | 17. (D)         |         |               |         |
| 18. (C)                                                                                      | 19. (B)      | 20. (A) $\rightarrow$ P,S; (B) $\rightarrow$ Q,S; (C) $\rightarrow$ R,T; (D) $\rightarrow$ Q, T | 21. (A)         |         |               |         |
| 22. (A,C,D)                                                                                  | 23. (B,C,D)  | 24. (B)                                                                                         | 25. (A)         | 26. (C) | 27. (A,C,D)   | 28. (C) |
| 29. (A,C,D)                                                                                  | 30. (D)      | 31. (D)                                                                                         | 32. (A)         | 33. (7) | 34. (6) / (7) | 35. (B) |
| 36. (D)                                                                                      | 37. (A, B)   | 38. (C,D)                                                                                       | 39. (A OR A, C) | 40. (A) | 41. (A)       |         |
| 42. (A,B,D)                                                                                  | 43. (B,D)    | 44. (A)                                                                                         |                 |         |               |         |

## HEATING EFFECTS

### 1. HEATING EFFECT OF CARBONATE & BICARBONATE SALTS :

(a) *Heating effect of carbonate salts :*

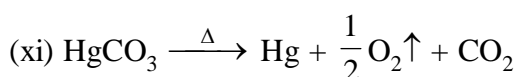
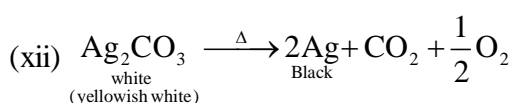
Metal carbonate  $\xrightarrow{\Delta}$  metal oxide +  $\text{CO}_2\uparrow$

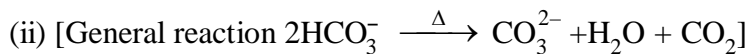
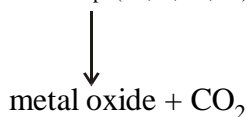
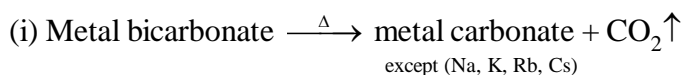


(ix) All carbonates **except** (Na, K, Rb, Cs) decompose on heating giving  $\text{CO}_2$

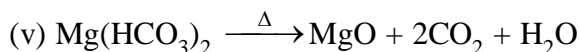
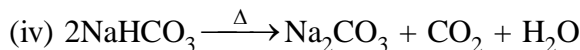
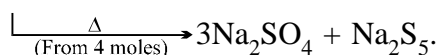
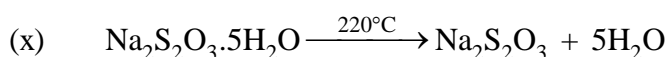
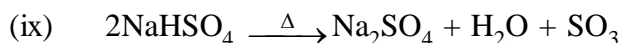
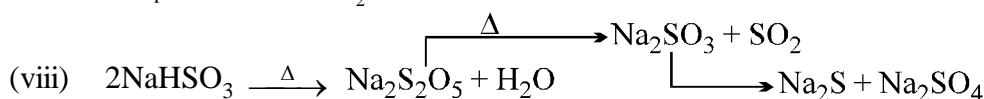
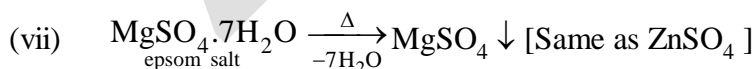
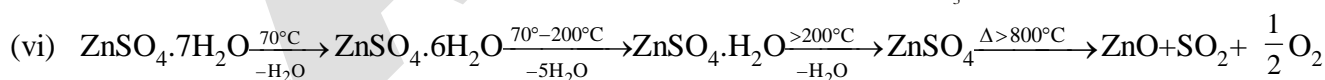
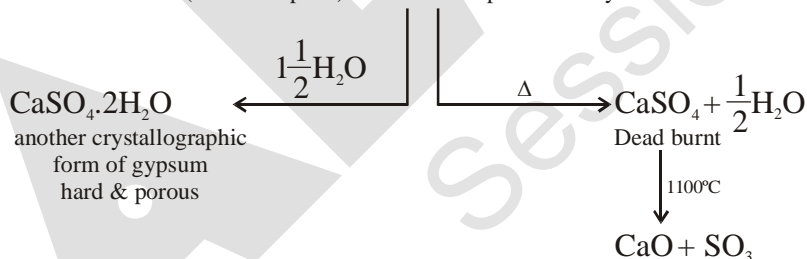
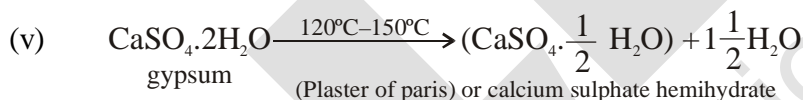
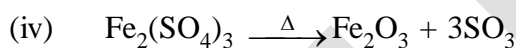
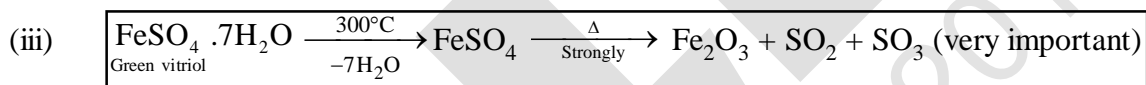
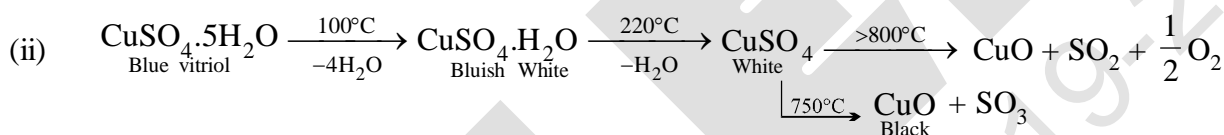
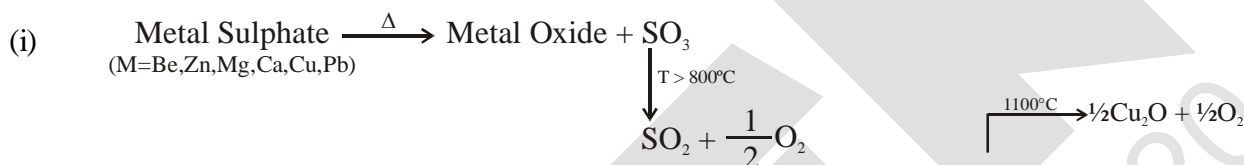
(x) Carbonates salts of (Na, K, Rb, Cs) do not decompose on heating, they are melt on high temperature.

(xi) Oxides of heavier metals are less stable so further decompose into metal & oxygen

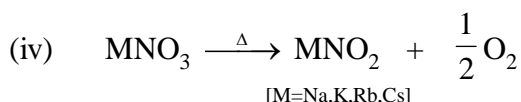
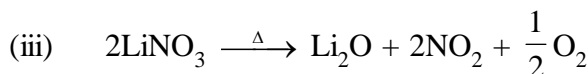
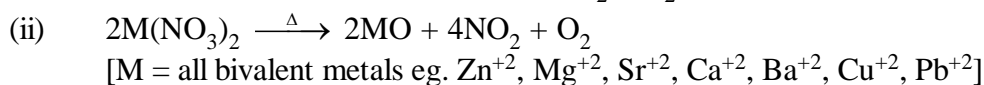
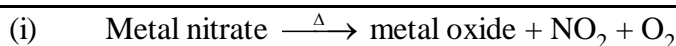


**(b) Heating effect of bicarbonate :**

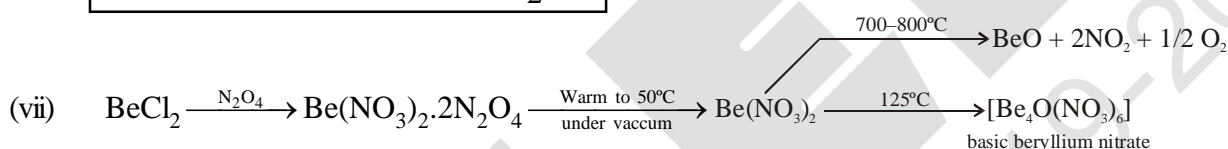
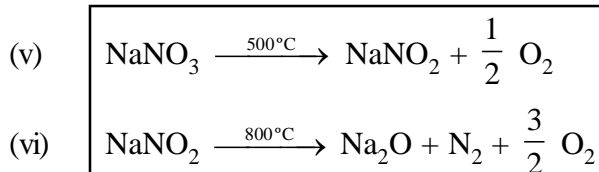
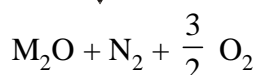
(iii) All bicarbonates decompose to give carbonates and  $\text{CO}_2$ . eg.

**2. HEATING EFFECT OF HYDRATED SULPHATE SALTS :**

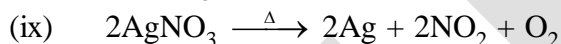
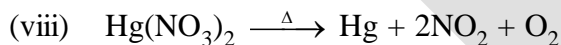
### 3. HEATING EFFECT OF NITRATE SALTS



high temperature

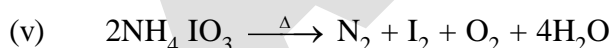
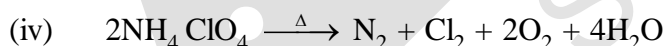
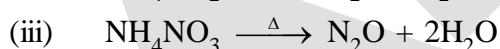
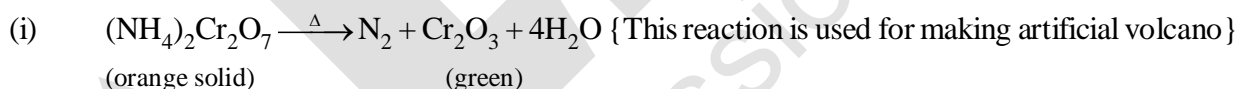


**Exception :** If formed oxide is of heavier metal then it being less stable and further decomposed in to metal and oxygen.

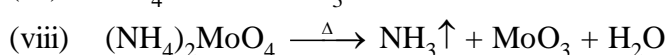
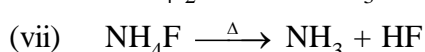
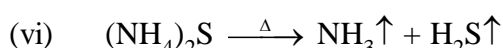
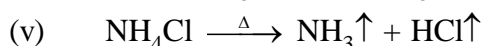
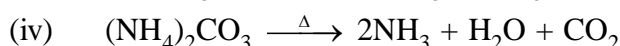
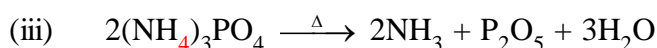
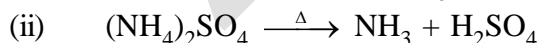
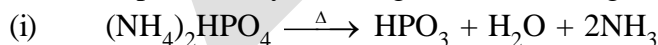


### 4. HEATING EFFECT OF AMMONIUM SALTS :

If anionic part is oxidising in nature, then N<sub>2</sub> will be the product (some times N<sub>2</sub>O).



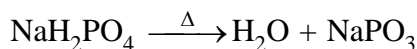
If anionic part weakly oxidising or non oxidising in nature then NH<sub>3</sub> will be the product.



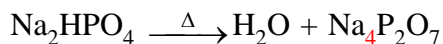


**5. HEATING EFFECT OF PHOSPHATE SALTS :**

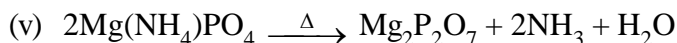
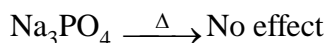
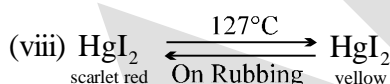
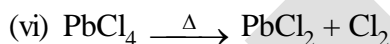
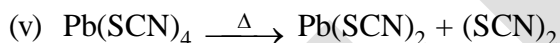
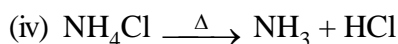
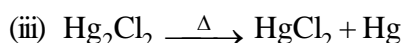
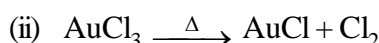
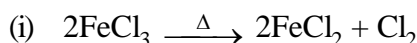
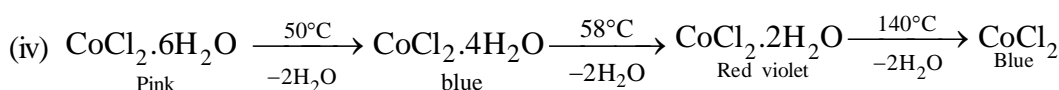
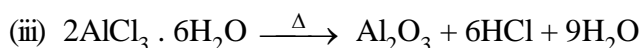
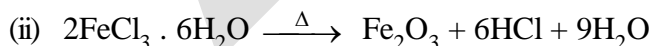
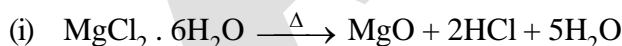
- (i) 1° Phosphate salts gives metaphosphate salt on heating.



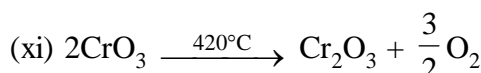
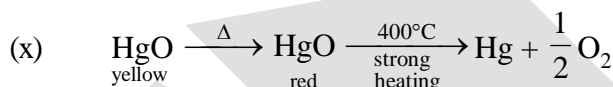
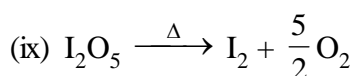
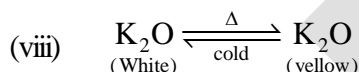
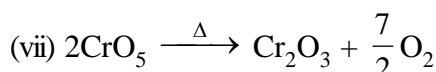
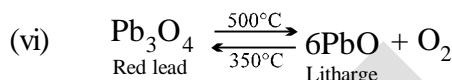
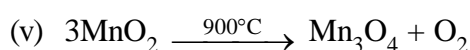
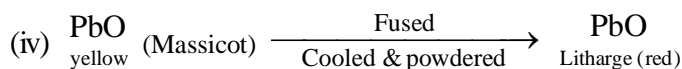
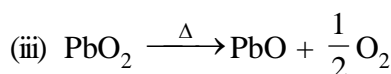
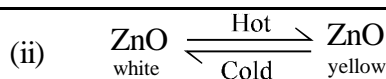
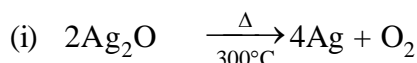
- (ii) 2° Phosphate salts gives pyrophosphate



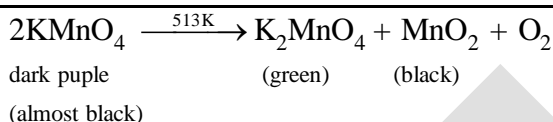
- (iii) 3° Phosphate salt have no heating effect

**6. HEATING EFFECT OF HALIDES SALTS :****7. HEATING EFFECT OF HYDRATED CHLORIDE SALTS**Hydrated  $\text{Co}^{2+}$  salt - PinkAnhydrous  $\text{Co}^{2+}$  salt - Blue

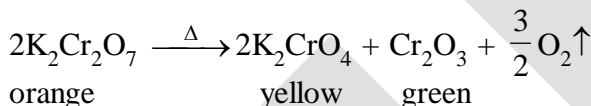
## 8. HEATING EFFECT OF OXIDE :



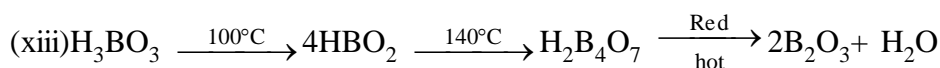
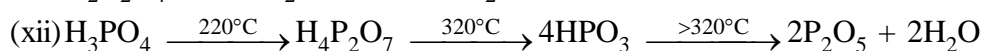
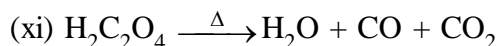
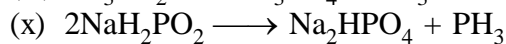
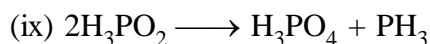
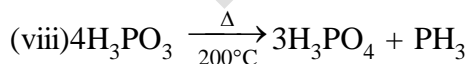
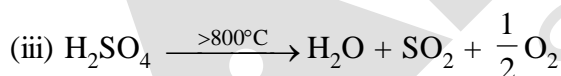
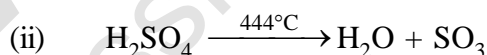
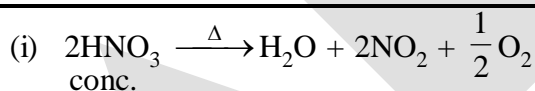
## 9. HEATING EFFECT OF PERMANGANATE :



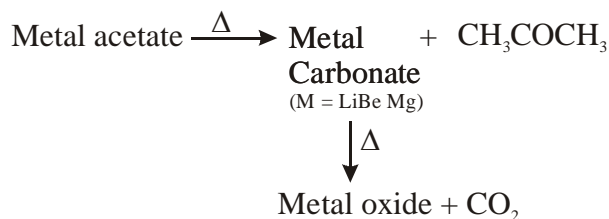
## 10. HEATING EFFECT OF DICHROMATE & CHROMATE SALTS :



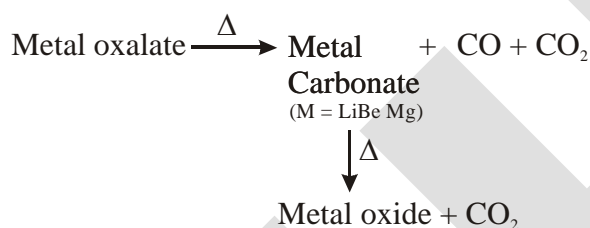
## 11. HEATING EFFECT OF ACIDS :



Undergoes  
dispropor-  
-tionation  
reaction

**12. HEATING EFFECTS OF ACETATE SALTS**

- (i)  $\text{Pb}(\text{OAc})_2 \xrightarrow{\Delta} \text{PbO} + \text{CO}_2 + \text{CH}_3\text{COCH}_3$   
 (ii)  $\text{Mg}(\text{OAc})_2 \xrightarrow{\Delta} \text{MgO} + \text{CO}_2 + \text{CH}_3\text{COCH}_3$   
 (iii)  $\text{Be}(\text{OAc})_2 \xrightarrow{\Delta} \text{BeO} + \text{CO}_2 + \text{CH}_3\text{COCH}_3$   
 (iv)  $\text{Ca}(\text{OAc})_2 \xrightarrow{\Delta} \text{CaCO}_3 + \text{CH}_3\text{COCH}_3$   
 (v)  $\text{Ba}(\text{OAc})_2 \xrightarrow{\Delta} \text{BaCO}_3 + \text{CH}_3\text{COCH}_3$   
 (vi)  $\text{CH}_3\text{CO}_2\text{K} \xrightarrow{\Delta} \text{K}_2\text{CO}_3 + \text{CH}_3\text{COCH}_3$

**13. HEATING EFFECTS OF OXALATE SALTS**

- (i)  $7\text{Na}_2\text{C}_2\text{O}_4 \xrightarrow{\Delta} 7\text{Na}_2\text{CO}_3 + 2\text{CO}_2 + 3\text{CO} + 2\text{C}$   
 (ii)  $\text{SnC}_2\text{O}_4 \xrightarrow{\Delta} \text{SnO} + \text{CO}_2 + \text{CO}$   
 (iii)  $\text{FeC}_2\text{O}_4 \xrightarrow{\Delta} \text{FeO} + \text{CO} + \text{CO}_2$   
 (iv)  $\text{Ag}_2\text{C}_2\text{O}_4 \xrightarrow{\Delta} 2\text{Ag} + 2\text{CO}_2$   
 (v)  $\text{HgC}_2\text{O}_4 \xrightarrow{\Delta} \text{Hg} + 2\text{CO}_2$

**14. HEATING EFFECTS OF FORMATE SALTS**

- (i)  $\text{HCO}_2\text{Na} \xrightarrow{350^\circ\text{C}} \text{Na}_2\text{C}_2\text{O}_4 + \text{H}_2\uparrow$   
 (ii)  $\text{HCOOAg} \xrightarrow{\Delta} \text{HCOOH} + 2\text{Ag} + \frac{1}{2} \text{O}_2 + \text{CO}$   

$$\downarrow$$

$$\text{CO}_2$$
  
 (iii)  $(\text{HCOO})_2\text{Hg} \longrightarrow \text{HCOOH} + \text{Hg} + \frac{1}{2} \text{O}_2 + \text{CO}$   

$$\downarrow$$

$$\text{CO}_2$$

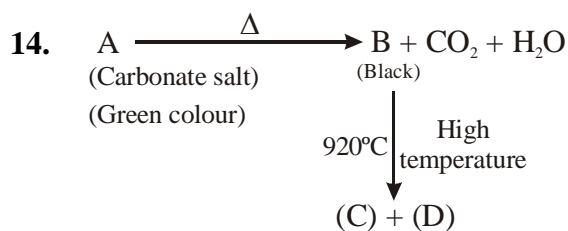
# EXERCISE

## Single correct

- Which of the following does not give metal oxide on heating  
(A)  $\text{NaCO}_3$  (B)  $\text{K}_2\text{CO}_3$  (C)  $\text{Rb}_2\text{CO}_3$  (D) All of these
- Which of the following metal bicarbonate will give metal oxide and  $\text{CO}_2$  on heating  
(A)  $\text{NaHCO}_3$  (B)  $\text{Mg}(\text{HCO}_3)_2$  (C)  $\text{KHCO}_3$  (D)  $\text{Rb}_2\text{CO}_3$
- Which of the following metal nitrate will give metal and oxygen on heating :  
(A)  $\text{KNO}_3$  (B)  $\text{NaNO}_3$  (C)  $\text{AgNO}_3$  (D)  $\text{RbNO}_3$
- Which of the following nitrate will give  $\text{N}_2\text{O}$  on heating :  
(A)  $\text{NH}_4\text{NO}_3$  (B)  $\text{NH}_4\text{NO}_2$  (C)  $\text{NaNO}_3$  (D)  $\text{AgNO}_3$
- Which of the following ammonium salt will not give acid on heating :  
(A)  $(\text{NH}_4)_2\text{HPO}_4$  (B)  $(\text{NH}_4)_2\text{MoO}_4$  (C)  $(\text{NH}_4)_2\text{SO}_4$  (D)  $\text{NH}_4\text{Cl}$
- Which of the following halide will not give halogen gas on heating :  
(A)  $\text{PbCl}_4$  (B)  $\text{PbBr}_4$  (C)  $\text{Hg}_2\text{Cl}_2$  (D) All of these
- Select the correct statements  
(A) Hydrated  $\text{Co}^{+2}$  salt is pink (B) Anhydrous  $\text{Co}^{+2}$  salt is of blue colour  
(C) Hybridisation of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  is  $\text{sp}^3\text{d}^2$  (D) All of these
- Which of the following metal sulphate will give  $\text{SO}_2$  and  $\text{SO}_3$  both gaseous product on heating :  
(A)  $\text{CuSO}_4$  (B)  $\text{FeSO}_4$  (C)  $\text{Fe}_2(\text{SO}_4)_3$  (D)  $\text{CaSO}_4$
- Which of the following compound is called dead burnt plaster :  
(A)  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  (B)  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (C)  $\text{CaSO}_4$  (anhy.) (D) None of these
- When  $\text{NaH}_2\text{PO}_4$  is heated then which of the following compound is formed :  
(A)  $\text{Na}_4\text{P}_2\text{O}_7$  (B)  $\text{Na}_3\text{PO}_4$  (C)  $\text{HPO}_3$  (D)  $\text{NaPO}_3$
- When  $\text{KMnO}_4$  is heated then which of the following compound is formed :  
(A)  $\text{K}_2\text{MnO}_4 + \text{MnO}_2$  (B)  $\text{K}_2\text{MnO}_4 + \text{MnO}$  (C)  $\text{MnO}_2 + \text{MnO}$  (D) No change
- When  $\text{CrO}_3$  is heated then ..... + ..... are formed :  
(A)  $\text{Cr}_2\text{O}_3$ ,  $\text{O}_2$  (B)  $\text{CrO}_2$ ,  $\text{O}_2$  (C)  $\text{Cr}_2\text{O}_7^{-2}$ ,  $\text{O}_2$  (D) None of these

## More than one may be correct

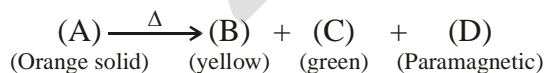
- Which of the following metal carbonate will give of metal and oxygen on heating-  
(A)  $\text{Ag}_2\text{CO}_3$  (B)  $\text{HgCO}_3$  (C)  $(\text{NH}_4)_2\text{CO}_3$  (D)  $\text{PbCO}_3$



Select the correct statements -

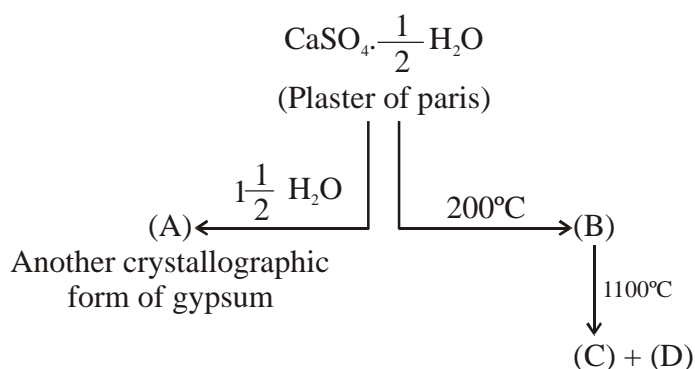
- (A) Compound (A) is basic copper carbonate  
 (B) Compound (B) CuO  
 (C) Compound (C) is  $\text{Cu}_2\text{O}$   
 (D) Compound (D) is paramagnetic in nature
15. When  $\text{Ag}_2\text{CO}_3$  is heated then product will be -  
 (A)  $\text{Ag}_2\text{O}$  (B) Ag (C)  $\text{O}_2$  (D)  $\text{CO}_2$
16. When compound A (orange red) is heated then green colour oxide of (B) is formed and inert gas (C) is formed then select the correct statements :  
 (A) Compound (A) is  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$   
 (B) Compound (B) is used in fire works  
 (C) Gas C is  $\text{N}_2$   
 (D) Heating effect of (A) is a type of intra molecular redox reaction
17. Which of the following hydrated salts will not become anhydrous on heating :  
 (A)  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  (B)  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (C)  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  (D)  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$
18. Which of the following metal nitrate produce  $\text{NO}_2$  on heating  
 (A)  $\text{Hg}(\text{NO}_3)_2$  (B)  $\text{RbNO}_3$  (C)  $\text{Pb}(\text{NO}_3)_2$  (D)  $\text{Cu}(\text{NO}_3)_2$
19. Which of the following oxides turns yellow on heating and becomes white on cooling :  
 (A) ZnO (B)  $\text{K}_2\text{O}$  (C) PbO (D)  $\text{Ag}_2\text{O}$

**Paragraph for Q. No. 20 to Q. No. 21**



20. Compound (A) is :  
 (A)  $\text{K}_2\text{Cr}_2\text{O}_7$  (B)  $\text{K}_2\text{CrO}_4$  (C)  $\text{Cr}_2\text{O}_3$  (D)  $\text{O}_2$
21. Compound (C) is also obtained on heating of :  
 (A)  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  (B)  $\text{NH}_4\text{ClO}_4$  (C)  $\text{NH}_4\text{NO}_3$  (D) None of these

Paragraph for Q. No. 22 & 23



22. Compound "A" is :

- (A)  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$       (B)  $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$       (C)  $\text{CaSO}_4 \cdot 3\text{H}_2\text{O}$       (D)  $\text{CaSO}_4 \cdot 5\text{H}_2\text{O}$

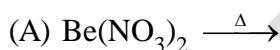
23. Compound "C" and "D" are respectively :

- (A)  $\text{CaO} + \text{CaSO}_4$       (B)  $\text{CaSO}_4 + \text{SO}_2$       (C)  $\text{CaSO}_4 + \text{SO}_3$       (D)  $\text{CaO} + \text{SO}_3$

Matrix match

24. Match the column

Column-I



Column-II

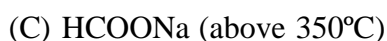
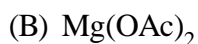
(P) Gives  $\text{H}_2\text{O}$

(Q) Oxyacid is obtained

(R) Gives disproportionation reaction

(S) Oxygen gas is evolved

25. Column-I (Compound)



Column-II (Products on heating)

(P)  $\text{CO}_2$  gas is evolved

(Q)  $\text{H}_2$  gas is evolved

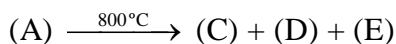
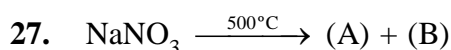
(R)  $\text{N}_2$  gas is evolved

(S) Same gas is evolved which is obtained by heating  $(\text{NH}_4)_2\text{SO}_4$

(T) Intra molecular redox reaction

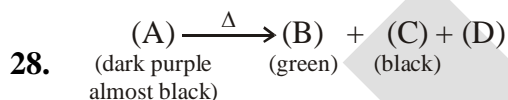
## Integer

26. When calamine is heated then a product (A) is formed then find the total number of following options are correct for compound (A) -
- (i) Compound (A) is white in cold conditions
  - (ii) Compound (A) is yellow in hot conditions
  - (iii) Compound (A) is called phillosopher's wool
  - (iv) Compound (A) when combined with CoO, then compound (B) is formed & colour of new compound (B) is green
  - (v) Compound (B) is called Rinmann's green



Find the number of correct statements

- (1) Compound (B) is paramagnetic in nature
- (2) Compound (B) when undergoes dimerisation then dimer product is diamagnetic in nature
- (3) Bond order of compound (B) is two
- (4) D is  $\text{N}_2$  gas
- (5) Compound B and E are same gas



Find the number of correct statements

- (1) Compound B is  $\text{K}_2\text{MnO}_4$
  - (2) Compound C is  $\text{MnO}_2$
  - (3) Compound D is  $\text{O}_2$
  - (4) Compound B is paramagnetic in nature
  - (5) Compound D has two unpaired electron in bonding molecular orbital
29. Total number of compounds undergoes disproportionation redox reaction on heating  $\text{MnO}_2$ ,  $\text{HOCl}$ ,  $\text{H}_3\text{PO}_3$ ,  $\text{HNO}_2$ ,  $\text{CrO}_5$ ,  $\text{HClO}_3$
30. On strong heating of  $\text{H}_3\text{PO}_4$  and  $\text{H}_3\text{BO}_3$ , sum of oxidation number of P & B in the final product obtained is

EXERCISE

|      |                                         |    |      |                                       |       |         |         |       |      |    |
|------|-----------------------------------------|----|------|---------------------------------------|-------|---------|---------|-------|------|----|
| Que. | 1                                       | 2  | 3    | 4                                     | 5     | 6       | 7       | 8     | 9    | 10 |
| Ans. | D                                       | B  | C    | A                                     | B     | C       | D       | B     | C    | D  |
| Que. | 11                                      | 12 | 13   | 14                                    | 15    | 16      | 17      | 18    | 19   | 20 |
| Ans. | A                                       | A  | A, B | A,B,C,D                               | B,C,D | A,B,C,D | A, B, C | A,C,D | A, B | A  |
| Que. | 21                                      | 22 | 23   | 24                                    |       |         |         |       |      |    |
| Ans. | A                                       | A  | D    | (A)→(S);(B)→(P,Q,R);(C)→(P);(D)→(Q,R) |       |         |         |       |      |    |
| Que. | 25                                      |    |      |                                       |       | 26      | 27      | 28    | 29   | 30 |
| Ans. | (A)→(R,T);(B)→(P);(C)→(P,Q,T);(D)→(P,S) |    |      |                                       |       | 5       | 4       | 4     | 4    | 8  |



## s-Block Element

### OBJECTIVES

After studying this unit you will be able to :

- Describe the general characteristics of the alkali metals and their compounds;
- Explain the general characteristics of the alkaline earth metals and their compounds;
- Describe the manufacture, properties and uses of industrially important sodium and calcium compounds including Portland cement ;
- Appreciate the biological significance of sodium, potassium, magnesium and calcium.

The *s*-block elements of the Periodic Table are those in which the last electron enters the outermost *s*-orbital. As the *s*-orbital can accommodate only two electrons, two groups (1 & 2) belong to the *s*-block of the Periodic Table. Group 1 of the Periodic Table consists of the elements: lithium, sodium, potassium, rubidium, caesium and francium. They are collectively known as the *alkali metals*. These are so called because they form hydroxides on reaction with water which are strongly alkaline in nature. The elements of Group 2 include beryllium, magnesium, calcium, strontium, barium and radium. These elements with the exception of beryllium are commonly known as the *alkaline earth metals*. These are so called because their oxides and hydroxides are alkaline in nature and these metal oxides are found in the earth's crust\*.

Among the alkali metals sodium and potassium are abundant and lithium, rubidium and caesium have much lower abundances. Francium is highly radioactive; its longest-lived isotope  $^{223}\text{Fr}$  has a half-life of only 21 minutes. Of the alkaline earth metals calcium and magnesium rank fifth and sixth in abundance respectively in the earth's crust. Strontium and barium have much lower abundances. Beryllium is rare and radium is the rarest of all comprising only 10–10 per cent of igneous rocks .

The general electronic configuration of *s*-block elements is [noble gas] $ns^1$  for alkali metals and [noble gas]  $ns^2$  for alkaline earth metals.

\* The thin, rocky outer layer of the Earth is crust. † A type of rock formed from magma (molten rock) that has cooled and hardened.

Lithium and beryllium, the first elements of Group 1 and Group 2 respectively exhibit some properties which are different from those of the other members of the respective group. In these anomalous properties they resemble the second element of the following group. Thus, lithium shows similarities to magnesium and beryllium to aluminium in many of their properties. This type of diagonal similarity is commonly referred to as *diagonal relationship* in the periodic table. The diagonal relationship is due to the similarity in ionic sizes and /or charge/radius ratio of the elements. Monovalent sodium and potassium ions and divalent magnesium and calcium ions are found in large proportions in biological fluids. These ions perform important biological functions such as maintenance of ion balance and nerve impulse conduction.

## 10.1 GROUP 1 ELEMENTS : ALKALI METALS

The alkali metals show regular trends in their physical and chemical properties with the increasing atomic number. The atomic, physical and chemical properties of alkali metals are discussed below.

### 10.1.1 Electronic Configuration

All the alkali metals have one valence electron,  $ns^1$  outside the noble gas core. The loosely held s-electron in the outermost valence shell of these elements makes them the most electropositive metals. They readily lose electron to give monovalent  $M^+$  ions. Hence they are never found in free state in nature.

| Element   | Symbol | Electronic configuration                                                           |
|-----------|--------|------------------------------------------------------------------------------------|
| Lithium   | Li     | $1s^2s^1$                                                                          |
| Sodium    | Na     | $1s^2 2s^2 2p^6 3s^1$                                                              |
| Potassium | K      | $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$                                                    |
| Rubidium  | Rb     | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^1$                                  |
| Caesium   | Cs     | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^6 5p^6 6s^1$ or [Xe] $6s^1$ |
| Francium  | Fr     | [Rn] $7s^1$                                                                        |

### 10.1.2 Atomic and Ionic Radii

$Li < Na < K < Rb < Cs$

Increase down the group, because value of  $n$  (principal quantum number) increases.

### 10.1.3 Ionization Enthalpy

$Li > Na > K > Rb > Cs$ .

This is because the effect of increasing size outweighs the increasing nuclear charge, and the outermost electron is very well screened from the nuclear charge.

### 10.1.4 Hydration Enthalpy

The hydration enthalpies of alkali metal ions decrease with increase in ionic sizes.

$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$

$Li^+$  has maximum degree of hydration and for this reason lithium salts are mostly hydrated, e.g.,  $LiCl \cdot 2H_2O$

### 10.1.5 Physical Properties

- All the alkali metals are silvery white, soft and light metals.
- Because of the large size, these elements have low density which increases down the group from Li to Cs. However, potassium is lighter than sodium.  
 $Li < K < Na < Rb < Cs$ .
- The melting and boiling points of the alkali metals are low indicating weak metallic bonding due to the presence of only a single valence electron in them.
- The alkali metals and their salts impart characteristic colour to an oxidizing flame. This is because the heat from the flame excites the outermost orbital electron to a higher energy level. When the excited electron comes back to the ground state, there is emission of radiation in the visible region as given below :

| Metal               | Li          | Na     | K      | Rb         | Cs    |
|---------------------|-------------|--------|--------|------------|-------|
| Colour              | Crimson red | Yellow | Violet | Red violet | Blue  |
| $\lambda/\text{nm}$ | 670.8       | 589.2  | 766.5  | 780.0      | 455.5 |

- (v) Alkali metals can therefore, be detected by the respective flame tests and can be determined by flame photometry or atomic absorption spectroscopy.
- (vi) These elements when irradiated with light, the light energy absorbed may be sufficient to make an atom lose electron.

**Table : Atomic and Physical Properties of the Alkali Metals**

| Property                                                           | Lithium<br>Li     | Sodium<br>Na       | Potassium K        | Rubidium<br>Rb     | Caesium<br>Cs      | Francium<br>Fr     |
|--------------------------------------------------------------------|-------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| Atomic number                                                      | 3                 | 11                 | 19                 | 37                 | 55                 | 87                 |
| Atomic mass ( $\text{g mol}^{-1}$ )                                | 6.94              | 22.99              | 39.10              | 85.47              | 132.91             | (223)              |
| Electronic configuration                                           | $[\text{He}]2s^1$ | $[\text{Ne}] 3s^1$ | $[\text{Ar}] 4s^1$ | $[\text{Kr}] 5s^1$ | $[\text{Xe}] 6s^1$ | $[\text{Rn}] 7s^1$ |
| Ionization enthalpy/ $\text{kJ mol}^{-1}$                          | 520               | 496                | 419                | 403                | 376                | ~375               |
| Hydration enthalpy/ $\text{kJ mol}^{-1}$                           | -506              | -406               | -330               | -310               | -276               | -                  |
| Metallic radius/pm                                                 | 152               | 186                | 227                | 248                | 265                | -                  |
| Ionic radius $\text{M}^+/\text{pm}$                                | 76                | 102                | 138                | 152                | 167                | (180)              |
| m.p./K                                                             | 454               | 371                | 336                | 312                | 302                | -                  |
| b.p./K                                                             | 1615              | 1156               | 1032               | 961                | 944                | -                  |
| Density / $\text{g cm}^{-3}$                                       | 0.53              | 0.97               | 0.86               | 1.53               | 1.90               | -                  |
| Standard Potentials $E^\circ/\text{V}$ for $(\text{M}^+/\text{M})$ | -3.04             | -2.714             | -2.925             | -2.930             | -2.927             | -                  |
| Occurrence in lithosphere                                          | 18*               | 2.27**             | 1.84**             | 78-12*             | 2-6*               | $\sim 10^{-18}$ *  |

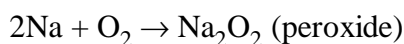
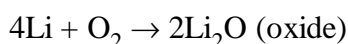
\*ppm (part per million), \*\*percentage by weight; † Lithosphere: The Earth's outer layer: its crust and part of the upper mantle.

This property makes caesium and potassium useful as electrodes in photoelectric cells.

### 10.1.6 Chemical Properties

The alkali metals are highly reactive due to their large size and low ionization enthalpy. The reactivity of these metals increases down the group.

- (i) **Reactivity towards air :** The alkali metals tarnish in dry air due to the formation of their oxides which in turn react with moisture to form hydroxides. They burn vigorously in oxygen forming oxides. Lithium forms monoxide, sodium forms peroxide, the other metals form superoxides. The superoxide  $\text{O}_2^-$  ion is stable only in the presence of large cations such as K, Rb, Cs.



In all these oxides the oxidation state of the alkali metal is +1. Lithium shows exceptional behaviour in reacting directly with nitrogen of air to form the nitride,  $\text{Li}_3\text{N}$  as well. Because of their high reactivity towards air and water, **alkali metals are normally kept in kerosene oil.**

### Problem 10.1

What is the oxidation state of K in  $\text{KO}_2$ ?

#### Solution

The superoxide species is represented as  $\text{O}_2^-$ ; since the compound is neutral, therefore, the oxidation state of potassium is +1.

(ii) **Reactivity towards water :** The alkali metals react with water to form hydroxide and dihydrogen.

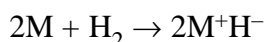


(M = an alkali metal)

It may be noted that although lithium has most negative  $E^\ominus$  value, its reaction with water is less vigorous than that of sodium which has the least negative  $E^\ominus$  value among the alkali metals. This behaviour of lithium is attributed to its small size and very high hydration energy. Other metals of the group react explosively with water.

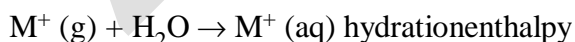
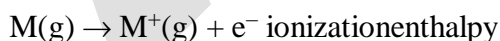
They also react with proton donors such as alcohol, gaseous ammonia and alkynes.

(iii) **Reactivity towards dihydrogen:** The alkali metals react with dihydrogen at about 673K (lithium at 1073K) to form hydrides. All the alkali metal hydrides are ionic solids with high melting points.



(iv) **Reactivity towards halogens :** The alkali metals readily react vigorously with halogens to form ionic halides,  $\text{M}+\text{X}-$ . However, lithium halides are somewhat covalent. It is because of the high polarisation capability of lithium ion (The distortion of electron cloud of the anion by the cation is called polarisation). The  $\text{Li}^+$  ion is very small in size and has high tendency to distort electron cloud around the negative halide ion. Since anion with large size can be easily distorted, among halides, lithium iodide is the most covalent in nature.

(v) **Reducing nature :** The alkali metals are strong reducing agents, lithium being the most and sodium the least powerful. The standard electrode potential ( $E^\ominus$ ) which measures the reducing power represents the overall change :



With the small size of its ion, lithium has the highest hydration enthalpy which accounts for its high negative  $E^\ominus$  value and its high reducing power.

### Problem 10.2

The  $E^\ominus$  for  $\text{Cl}_2/\text{Cl}^-$  is +1.36, for  $\text{I}_2/\text{I}^-$  is +0.53, for  $\text{Ag}^+/\text{Ag}$  is +0.79,  $\text{Na}^+/\text{Na}$  is -2.71 and for  $\text{Li}^+/\text{Li}$  is -3.04. Arrange the following ionic species in decreasing order of reducing strength :

$\text{I}^-$ ,  $\text{Ag}$ ,  $\text{Cl}^-$ ,  $\text{Li}$ ,  $\text{Na}$

## Solution

The order is  $\text{Li} > \text{Na} > \text{I}^- > \text{Ag} > \text{Cl}^-$

- (vi) **Solutions in liquid ammonia :** The alkali metals dissolve in liquid ammonia giving deep blue solutions which are conducting in nature.



The blue colour of the solution is due to the ammoniated electron which absorbs energy in the visible region of light and thus imparts blue colour to the solution. The solutions are paramagnetic and on standing slowly liberate hydrogen resulting in the formation of amide.

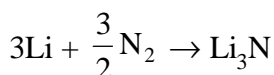
$\text{M}_{(\text{am})}^+ + \text{e}^- + \text{NH}_3(1) \rightarrow \text{MNH}_{2(\text{am})} + \frac{1}{2}\text{H}_2(\text{g})$  (where 'am' denotes solution in ammonia.) In concentrated solution, the blue colour changes to bronze colour and becomes diamagnetic.

- (vii) **Reaction with  $\text{H}_2$**

They react with  $\text{H}_2$  forming metal hydride with formula  $\text{MH}$  which are of ionic nature. Stability of hydride decreases down the group.

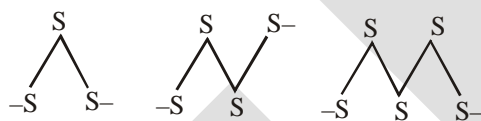
- (viii) **Reaction with  $\text{N}_2$**

Only Lithium reacts with  $\text{N}_2$  to form ionic lithium nitride  $\text{Li}_3\text{N}$ .

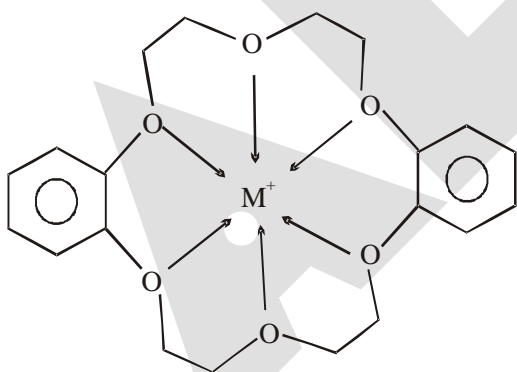


- (ix) **Sulphides**

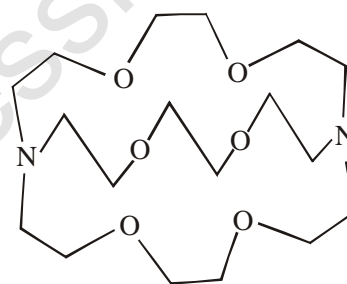
All metals react with S forming sulphides such as  $\text{Na}_2\text{S}$  and  $\text{Na}_2\text{S}_n$  ( $n = 2, 3, 4, 5$  or  $6$ ). The polysulphide ions are made from zig-zag chains of sulphur atoms.



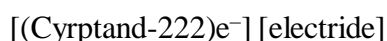
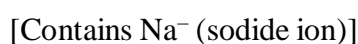
- (x) **Crown Ethers and Cryptands :**



Dibenzo-18-Crown-6



Cryptand - 222



## 10.1.7 Uses :

Lithium metal is used to make useful alloys, for example with lead to make 'white metal' bearings for motor engines, with aluminium to make aircraft parts, and with magnesium to make armour plates. It is used in thermonuclear reactions.

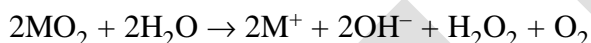
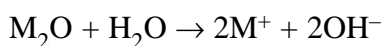
Lithium is also used to make electrochemical cells. Sodium is used to make a Na/Pb alloy needed to make  $\text{PbEt}_4$  and  $\text{PbMe}_4$ . These organolead compounds were earlier used as anti-knock additives to petrol, but nowadays vehicles use lead-free petrol. Liquid sodium metal is used as a coolant in fast breeder nuclear reactors. Potassium has a vital role in biological systems. Potassium chloride is used as a fertilizer. Potassium hydroxide is used in the manufacture of soft soap. It is also used as an excellent absorbent of carbon dioxide. Caesium is used in devising photoelectric cells.

## 10.2 GENERAL CHARACTERISTICS OF THE COMPOUNDS OF THE ALKALI METALS

All the common compounds of the alkali metals are generally ionic in nature. General characteristics of some of their compounds are discussed here.

### 10.2.1 Oxides and Hydroxides

On combustion in excess of air, lithium forms mainly the oxide,  $\text{Li}_2\text{O}$  (plus some peroxide  $\text{Li}_2\text{O}_2$ ), sodium forms the peroxide,  $\text{Na}_2\text{O}_2$  (and some oxide  $\text{Na}_2\text{O}$ ) whilst potassium, rubidium and caesium form the superoxides,  $\text{MO}_2$ . Under appropriate conditions pure compounds  $\text{M}_2\text{O}$ ,  $\text{M}_2\text{O}_2$  and  $\text{MO}_2$  may be prepared. The increasing stability of the peroxide or superoxide, as the size of the metal ion increases, is due to the stabilisation of large anions by larger cations through lattice energy effects. These oxides are easily hydrolysed by water to form the hydroxides according to the following reactions :



The oxides and the peroxides are colourless when pure, but the superoxides are yellow or orange in colour. The superoxides are also paramagnetic. Sodium peroxide is widely used as an oxidising agent in inorganic chemistry.

### Problem 10.3

Why is  $\text{KO}_2$  paramagnetic ?

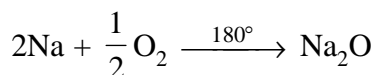
### Solution

The superoxide  $\text{O}_2^-$  is paramagnetic because of one unpaired electron in  $\pi^*2p$  molecular orbital. The hydroxides which are obtained by the reaction of the oxides with water are all white crystalline solids. The alkali metal hydroxides are the strongest of all bases and dissolve freely in water with evolution of much heat on account of intense hydration.

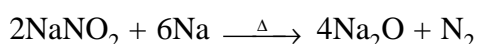
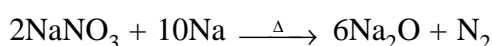
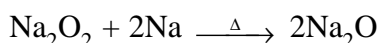
### Sodium Oxide ( $\text{Na}_2\text{O}$ ) :

#### Preparation :

- (i) It is obtained by burning sodium at  $180^\circ\text{C}$  in a limited supply of air or oxygen and distilling off the excess of sodium in vacuum.

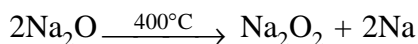


- (ii) By heating sodium peroxide, nitrate or nitrite with sodium.

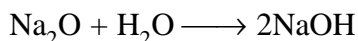


**Properties :**

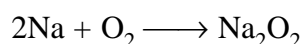
- (i) It is white amorphous mass.  
 (ii) It decomposes at 400°C into sodium peroxide and sodium



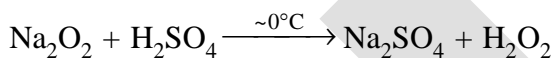
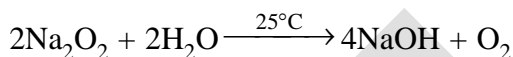
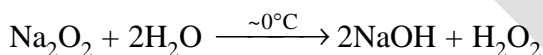
- (iii) It dissolve violently in water, yielding caustic soda.

**Sodium Peroxides ( $\text{Na}_2\text{O}_2$ ) :**

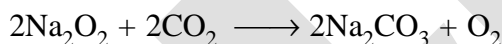
**Preparation:** It is formed by heating the metal in excess of air or oxygen at 300°, which is free from moisture and  $\text{CO}_2$ .

**Properties:**

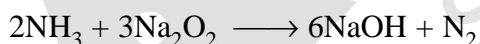
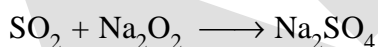
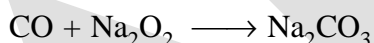
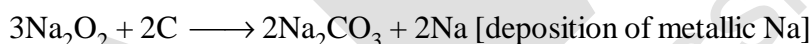
- (i) It is a pale yellow solid, becoming white in air from the formation of a film of  $\text{NaOH}$  and  $\text{Na}_2\text{CO}_3$ .  
 (ii) In cold water ( $\sim 0^\circ\text{C}$ ) produces  $\text{H}_2\text{O}_2$  but at room temperature produces  $\text{O}_2$ . In ice-cold mineral acids also produces  $\text{H}_2\text{O}_2$ .



- (iii) It reacts with  $\text{CO}_2$ , giving sodium carbonate and oxygen and hence its use for purifying air in a confined space e.g. submarine, ill-ventilated room,



- (iv) It is an oxidising agent and oxidises charcoal,  $\text{CO}$ ,  $\text{NH}_3$ ,  $\text{SO}_2$ .



- (v) It contains peroxide ion  $[\text{O}-\text{O}]^{-2}$

**Uses:**

- (i) For preparing  $\text{H}_2\text{O}_2$ ,  $\text{O}_2$   
 (ii) Oxygenating the air in submarines  
 (iii) Oxidising agent in the laboratory.

**Oxides of Potassium :**

and



Colours : White

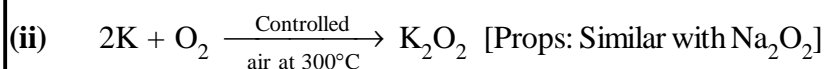
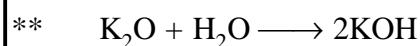
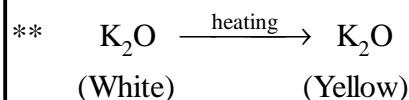
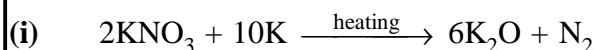
White

Red

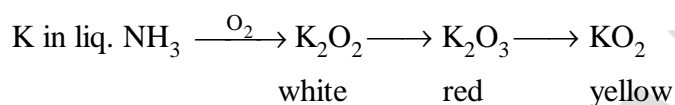
Bright Yellow

Orange Solid

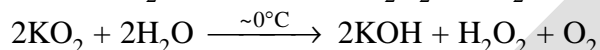
**Preparation :**



(iii) Passage of  $\text{O}_2$  through a blue solution of K in liquid  $\text{NH}_3$  yields oxides  $\text{K}_2\text{O}_2$  (white),  $\text{K}_2\text{O}_3$  (red) and  $\text{KO}_2$  (deep yellow) i.e

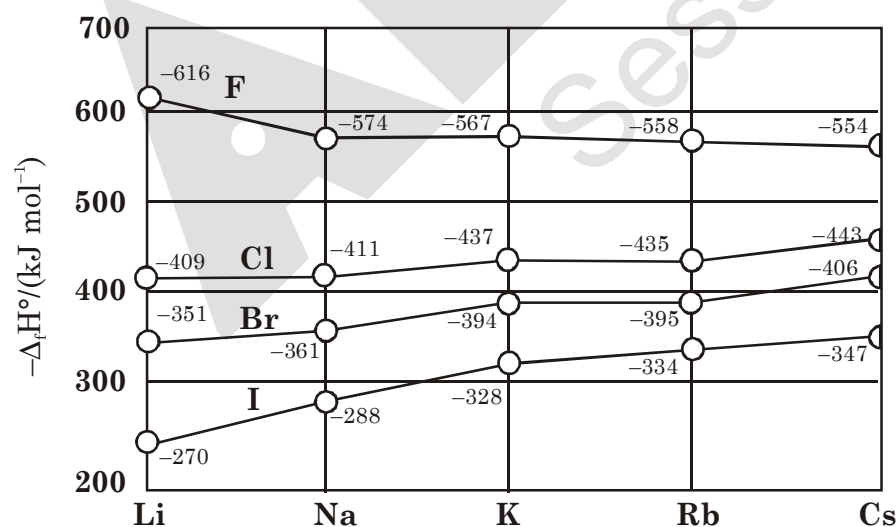


\*\*  $\text{KO}_2$  reacts with  $\text{H}_2\text{O}$  and produces  $\text{H}_2\text{O}_2$  and  $\text{O}_2$  both



**10.2.2 Halides**

The alkali metal halides,  $\text{MX}$ , ( $\text{X}=\text{F}, \text{Cl}, \text{Br}, \text{I}$ ) are all high melting, colourless crystalline solids. They can be prepared by the reaction of the appropriate oxide, hydroxide or carbonate with aqueous hydrohalic acid ( $\text{HX}$ ). All of these halides have high negative enthalpies of formation; the  $\Delta_f H^\ominus$  values for fluorides become less negative as we go down the group, whilst the reverse is true for  $\Delta_f H^\ominus$  for chlorides, bromides and iodides. For a given metal  $\Delta_f H^\ominus$  always becomes less negative from fluoride to iodide.



The standard enthalpies of formation of the halides of Group 1 elements at 298 K



### 10.2.3 Salts of Oxo-Acids

Oxo-acids are those in which the acidic proton is on a hydroxyl group with an oxo group attached to the same atom e.g., carbonic acid,  $\text{H}_2\text{CO}_3$  ( $\text{OC}(\text{OH})_2$ ); sulphuric acid,  $\text{H}_2\text{SO}_4$  ( $\text{O}_2\text{S}(\text{OH})_2$ ). The alkali metals form salts with all the oxo-acids. They are generally soluble in water and thermally stable.

Their carbonates ( $\text{M}_2\text{CO}_3$ ) and in most cases the hydrogencarbonates ( $\text{MHCO}_3$ ) also are highly stable to heat. As the electropositive character increases down the group, the stability of the carbonates and hydrogencarbonates increases. Lithium carbonate is not so stable to heat; lithium being very small in size polarises a large  $\text{CO}_3^{2-}$  ion leading to the formation of more stable  $\text{Li}_2\text{O}$  and  $\text{CO}_2$ . Its hydrogencarbonate does not exist as a solid.

### 10.3 ANOMALOUS PROPERTIES OF LITHIUM

The anomalous behaviour of lithium is due to the : (i) exceptionally small size of its atom and ion, and (ii) high polarising power (i.e., charge/ radius ratio). As a result, there is increased covalent character of lithium compounds which is responsible for their solubility in organic solvents. Further, lithium shows diagonal relationship to magnesium which has been discussed subsequently.

#### 10.3.1 Points of Difference between Lithium and other Alkali Metals

- (i) Lithium is much harder. Its m.p. and b.p. are higher than the other alkali metals.
- (ii) Lithium is least reactive but the strongest reducing agent among all the alkali metals. On combustion in air it forms mainly monoxide,  $\text{Li}_2\text{O}$  and the nitride,  $\text{Li}_3\text{N}$  unlike other alkali metals.
- (iii)  $\text{LiCl}$  is deliquescent and crystallises as a hydrate,  $\text{LiCl} \cdot 2\text{H}_2\text{O}$  whereas other alkali metal chlorides do not form hydrates.
- (iv) Lithium hydrogencarbonate is not obtained in the solid form while all other elements form solid hydrogencarbonates.
- (v) Lithium unlike other alkali metals forms no ethynide on reaction with ethyne.
- (vi) Lithium nitrate when heated gives lithium oxide,  $\text{Li}_2\text{O}$ , whereas other alkali metal nitrates decompose to give the corresponding nitrite.  

$$4\text{LiNO}_3 \rightarrow 2\text{Li}_2\text{O} + 4\text{NO}_2 + \text{O}_2$$

$$2\text{NaNO}_3 \rightarrow 2\text{NaNO}_2 + \text{O}_2$$
- (vii)  $\text{LiF}$  and  $\text{Li}_2\text{O}$  are comparatively much less soluble in water than the corresponding compounds of other alkali metals.

#### 10.3.2 Points of Similarities between Lithium and Magnesium

The similarity between lithium and magnesium is particularly striking and arises because of their similar sizes : atomic radii,  $\text{Li} = 152 \text{ pm}$ ,  $\text{Mg} = 160 \text{ pm}$ ; ionic radii :  $\text{Li}^+ = 76 \text{ pm}$ ,  $\text{Mg}^{2+} = 72 \text{ pm}$ . The main points of similarity are :

- (i) Both lithium and magnesium are harder and lighter than other elements in the respective groups.
- (ii) Lithium and magnesium react slowly with water. Their oxides and hydroxides are much less soluble and their hydroxides decompose on heating. Both form a nitride,  $\text{Li}_3\text{N}$  and  $\text{Mg}_3\text{N}_2$ , by direct combination with nitrogen.
- (iii) The oxides,  $\text{Li}_2\text{O}$  and  $\text{MgO}$  do not combine with excess oxygen to give any superoxide.
- (iv) The carbonates of lithium and magnesium decompose easily on heating to form the oxides and  $\text{CO}_2$ . Solid hydrogencarbonates are not formed by lithium and magnesium.
- (v) Both  $\text{LiCl}$  and  $\text{MgCl}_2$  are soluble in ethanol.
- (vi) Both  $\text{LiCl}$  and  $\text{MgCl}_2$  are deliquescent and crystallise from aqueous solution as hydrates,  $\text{LiCl} \cdot 2\text{H}_2\text{O}$  and  $\text{MgCl}_2 \cdot 8\text{H}_2\text{O}$ .

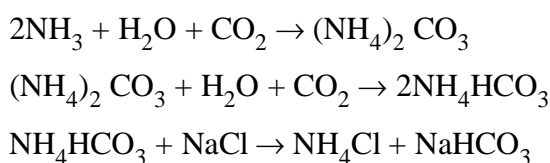
## 10.4 SOME IMPORTANT COMPOUNDS OF SODIUM

Industrially important compounds of sodium include sodium carbonate, sodium hydroxide, sodium chloride and sodium bicarbonate. The large scale production of these compounds and their uses are described below :

**Sodium Carbonate (Washing Soda),  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$** 

Sodium carbonate is generally prepared by **Solvay Process**. In this process, advantage is taken of the low solubility of sodium hydrogencarbonate whereby it gets precipitated in the reaction of sodium chloride with ammonium hydrogencarbonate. The latter is prepared by passing  $\text{CO}_2$  to a concentrated solution of sodium chloride saturated with ammonia, where ammonium carbonate followed by ammonium hydrogencarbonate are formed.

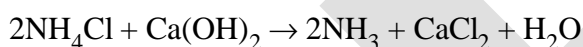
The equations for the complete process may be written as:



Sodium hydrogencarbonate crystal separates. These are heated to give sodium carbonate.

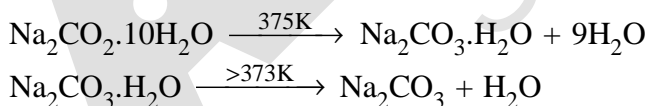


In this process  $\text{NH}_3$  is recovered when the solution containing  $\text{NH}_4\text{Cl}$  is treated with  $\text{Ca}(\text{OH})_2$ . Calcium chloride is obtained as a by-product.

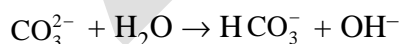


It may be mentioned here that Solvay process cannot be extended to the manufacture of potassium carbonate because potassium hydrogencarbonate is too soluble to be precipitated by the addition of ammonium hydrogencarbonate to a saturated solution of potassium chloride.

**Properties :** Sodium carbonate is a white crystalline solid which exists as a decahydrate,  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ . This is also called washing soda. It is readily soluble in water. On heating, the decahydrate loses its water of crystallisation to form monohydrate. Above 373K, the monohydrate becomes completely anhydrous and changes to a white powder called soda ash.



Carbonate part of sodium carbonate gets hydrolysed by water to form an alkaline solution.



- Uses:**
- (i) It is used in water softening, laundering and cleaning.
  - (ii) It is used in the manufacture of glass, soap, borax and caustic soda.
  - (iii) It is used in paper, paints and textile industries.
  - (iv) It is an important laboratory reagent both in qualitative and quantitative analysis.

**Note:**  $\text{K}_2\text{CO}_3$  cannot be prepared by **Solvay process** because  $\text{KHCO}_3$  is soluble in water and cannot be separated from  $\text{NH}_4\text{Cl}$ .

**Sodium Chloride, NaCl**

The most abundant source of sodium chloride is sea water which contains 2.7 to 2.9% by mass of the salt. In tropical countries like India, common salt is generally obtained by evaporation of sea water. Approximately 50 lakh tons of salt are produced annually in India by solar evaporation. Crude sodium chloride, generally obtained by crystallisation of brine solution, contains sodium sulphate, calcium sulphate, calcium chloride and magnesium chloride as impurities. Calcium chloride,  $\text{CaCl}_2$ , and magnesium chloride,  $\text{MgCl}_2$  are impurities because they are deliquescent (absorb moisture easily from the atmosphere).

To obtain pure sodium chloride, the crude salt is dissolved in minimum amount of water and filtered to remove insoluble impurities. The solution is then saturated with hydrogen chloride gas. Crystals of pure sodium chloride separate out. Calcium and magnesium chloride, being more soluble than sodium chloride, remain in solution.

Sodium chloride melts at 1081 K. It has a solubility of 36.0 g in 100 g of water at 273 K. The solubility does not increase appreciably with increase in temperature.

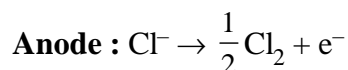
**Uses :**

- (i) It is used as a common salt or table salt for domestic purpose.
- (ii) It is used for the preparation of  $\text{Na}_2\text{O}_2$ ,  $\text{NaOH}$  and  $\text{Na}_2\text{CO}_3$ .
- (iii) It is used to prepare freezing mixture in laboratory [Ice-common salt mixture is called freezing mixture and temperature goes down to  $-23^\circ\text{C}$ .]
- (iv) For melting ice and snow on road.

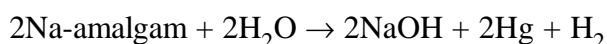
**Sodium Hydroxide (Caustic Soda), NaOH**

Sodium hydroxide is generally prepared commercially by the electrolysis of sodium chloride in Castner-Kellner cell. A brine solution is electrolysed using a mercury cathode and a carbon anode. Sodium metal discharged at the cathode combines with mercury to form sodium amalgam. Chlorine gas is evolved at

the anode. **Cathode :**  $\text{Na}^+ + \text{e}^- \xrightarrow{\text{Hg}} \text{Na} - \text{amalgam}$



The amalgam is treated with water to give sodium hydroxide and hydrogen gas.



Sodium hydroxide is a white, translucent solid. It melts at 591 K. It is readily soluble in water to give a strong alkaline solution. Crystals of sodium hydroxide are deliquescent. The sodium hydroxide solution at the surface reacts with the  $\text{CO}_2$  in the atmosphere to form  $\text{Na}_2\text{CO}_3$ .

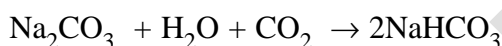
**Uses :** It is used in

- (i) The manufacture of soap, paper, artificial silk and a number of chemicals,
- (ii) In petroleum refining,
- (iii) In the purification of bauxite,
- (iv) In the textile industries for mercerising cotton fabrics, (v) for the preparation of pure fats and oils, and
- (vi) As a laboratory reagent.

### **Sodium Hydrogencarbonate (Baking Soda), $\text{NaHCO}_3$**

Sodium hydrogencarbonate is known as baking soda because it decomposes on heating to generate bubbles of carbon dioxide (leaving holes in cakes or pastries and making them light and fluffy).

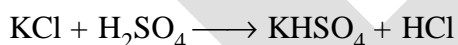
Sodium hydrogencarbonate is made by saturating a solution of sodium carbonate with carbon dioxide. The white crystalline powder of sodium hydrogencarbonate, being less soluble, gets separated out.



Sodium hydrogencarbonate is a mild antiseptic for skin infections. **It is used in fire extinguishers.**

### **Potassium carbonate, $\text{K}_2\text{CO}_3$**

It is also called potash or pearl ash. It cannot be made by the use of solvay process as potassium bicarbonate is more soluble than sodium bicarbonate. However, it can be prepared by **Le-Blanc process**. KCl is first converted into  $\text{K}_2\text{SO}_4$ . Potassium sulphate ( $\text{K}_2\text{SO}_4$ ) is then heated with  $\text{CaCO}_3$  and carbon.



It is a white powder, deliquescent in nature. It is highly soluble in water.

**Uses :** It is used in the manufacture of hard glass. The mixture of  $\text{K}_2\text{CO}_3$  and  $\text{Na}_2\text{CO}_3$  is used as a **fusion mixture** in laboratory.

## **10.5 BIOLOGICAL IMPORTANCE OF SODIUM AND POTASSIUM**

A typical 70 kg man contains about 90 g of Na and 170 g of K compared with only 5 g of iron and 0.06 g of copper. Sodium ions are found primarily on the outside of cells, being located in blood plasma and in the interstitial fluid which surrounds the cells. These ions participate in the transmission of nerve signals, in regulating the flow of water across cell membranes and in the transport of sugars and amino acids into cells. Sodium and potassium, although so similar chemically, differ quantitatively in their ability to penetrate cell membranes, in their transport mechanisms and in their efficiency to activate enzymes.

Thus, potassium ions are the most abundant cations within cell fluids, where they activate many enzymes, participate in the oxidation of glucose to produce ATP and, with sodium, are responsible for the transmission of nerve signals.

There is a very considerable variation in the concentration of sodium and potassium ions found on the opposite sides of cell membranes. As a typical example, in blood plasma, sodium is present to the extent of  $143 \text{ mmolL}^{-1}$ , whereas the potassium level is only  $5 \text{ mmolL}^{-1}$  within the red blood cells. These concentrations change to  $10 \text{ mmolL}^{-1}$  ( $\text{Na}^+$ ) and  $105 \text{ mmolL}^{-1}$  ( $\text{K}^+$ ). These ionic gradients demonstrate that a discriminatory mechanism, called the sodium-potassium pump, operates across the cell membranes which consumes more than one-third of the ATP used by a resting animal and about 15 kg per 24 h in a resting human.

## 10.6 GROUP 2 ELEMENTS : ALKALINE EARTH METALS

The group 2 elements comprise beryllium, magnesium, calcium, strontium, barium and radium. They follow alkali metals in the periodic table. These (except beryllium) are known as alkaline earth metals. The first element beryllium differs from the rest of the members and shows diagonal relationship to aluminium. The atomic and physical properties of the alkaline earth metals are shown in Table.

### 10.6.1 Electronic Configuration

These elements have two electrons in the  $s$ -orbital of the valence shell. Their general electronic configuration may be represented as [noble gas]  $ns^2$ . Like alkali metals, the compounds of these elements are also predominantly ionic.

| Element   | Symbol | Electronic configuration                                                                  |
|-----------|--------|-------------------------------------------------------------------------------------------|
| Beryllium | Be     | $1s^2 2s^2$                                                                               |
| Magnesium | Mg     | $1s^2 2s^2 2p^6 3s^2$                                                                     |
| Calcium   | Ca     | $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$                                                           |
| Strontium | Sr     | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$                                         |
| Barium    | Ba     | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^2$ or $[\text{Xe}] 6s^2$ |
| Radium    | Ra     | $[\text{Rn}] 7s^2$                                                                        |

## 10.6.2 Atomic and Ionic Radii

The atomic and ionic radii of the alkaline earth metals are smaller than those of the

**Table : Atomic and Physical Properties of the Alkaline Earth Metals**

| Property                                                                | Beryllium<br>Be   | Magnesium<br>Mg    | Calcium<br>Ca      | Strontium<br>Sr    | Barium<br>Ba       | Radium<br>Ra       |
|-------------------------------------------------------------------------|-------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| Atomic number                                                           | 4                 | 12                 | 20                 | 38                 | 56                 | 88                 |
| Atomic mass ( $\text{g mol}^{-1}$ )                                     | 9.01              | 24.31              | 40.08              | 87.62              | 137.33             | 226.03             |
| Electronic configuration                                                | $[\text{He}]2s^2$ | $[\text{Ne}] 3s^2$ | $[\text{Ar}] 4s^2$ | $[\text{Kr}] 5s^2$ | $[\text{Xe}] 6s^2$ | $[\text{Rn}] 7s^2$ |
| Ionization enthalpy (I)/ $\text{kJ mol}^{-1}$                           | 899               | 737                | 590                | 549                | 503                | 509                |
| Ionization enthalpy(II) $\text{kJ mol}^{-1}$                            | 1757              | 1450               | 1145               | 1064               | 965                | 979                |
| Hydration enthalpy/ $\text{kJ mol}^{-1}$                                | -2494             | -1921              | -1577              | -1443              | -1305              | -                  |
| Metallic radius/pm                                                      | 111               | 160                | 197                | 215                | 222                | -                  |
| Ionic radius $\text{M}^+/\text{pm}$                                     | 31                | 72                 | 100                | 118                | 135                | 148                |
| m.p./K                                                                  | 1560              | 924                | 1124               | 1062               | 1002               | 973                |
| b.p./K                                                                  | 2745              | 1363               | 1767               | 1655               | 2078               | (1973)             |
| Density / $\text{g cm}^{-3}$                                            | 1.84              | 1.74               | 1.55               | 2.63               | 3.59               | (5.5)              |
| Standard Potentials $E^\circ / \text{V}$ for $(\text{M}^{+2}/\text{M})$ | -1.97             | -2.36              | -2.84              | -2.89              | -2.92              | -2.92              |
| Occurrence in lithosphere                                               | 2*                | 2.76**             | 4.6**              | 384*               | 390*               | $10^{-6}$ *        |

\*ppm (part per million); \*\* percentage by weight :

Corresponding alkali metals in the same periods. This is due to the increased nuclear charge in these elements. Within the group, the atomic and ionic radii increase with increase in atomic number.

## 10.6.3 Ionization Enthalpies

**Ionization Enthalpy**

$\text{Be} > \text{Mg} > \text{Ca} > \text{Sr} > \text{Ba}$

Down the group IE decreases due to increase in size

Q.  $\text{IE}_1$  of AM  $<$   $\text{IE}_1$  of AEM

$\text{IE}_2$  of AM  $>$   $\text{IE}_2$  of AEM

[where AM = Alkali metal, AEM = Alkaline earth metal]

**Reason :**  $\text{IE}_1$  of AEM is large due to increased nuclear charge in AEM as compared to AM but  $\text{IE}_2$  of AM is large because second electron in AM is to be removed from cation which has already acquired noble gas configuration.

## 10.6.4 Hydration Enthalpies

Like alkali metal ions, the hydration enthalpies of alkaline earth metal ions decrease with increase in ionic size down the group.

$\text{Be}^{2+} > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$

The hydration enthalpies of alkaline earth metal ions are larger than those of alkali metal ions. Thus, compounds of alkaline earth metals are more extensively hydrated than those of alkali metals, e.g.,  $\text{MgCl}_2$  and  $\text{CaCl}_2$  exist as  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  while  $\text{NaCl}$  and  $\text{KCl}$  do not form such hydrates.

### 10.6.5 Physical Properties

- (i) The alkaline earth metals, in general, are silvery white, lustrous and relatively soft but harder than the alkali metals. Beryllium and magnesium appear to be somewhat greyish.
- (ii) The melting and boiling points of these metals are higher than the corresponding alkali metals due to smaller sizes. The trend is, however, not systematic.
- (iii) Because of the low ionisation enthalpies, they are strongly electropositive in nature. The electropositive character increases down the group from Be to Ba.
- (iv) Calcium, strontium and barium impart characteristic brick red, crimson and apple green colours respectively to the flame. In flame the electrons are excited to higher energy levels and when they drop back to the ground state, energy is emitted in the form of visible light. The electrons in beryllium and magnesium are too strongly bound to get excited by flame. Hence, these elements do not impart any colour to the flame. The flame test for Ca, Sr and Ba is helpful in their detection in qualitative analysis and estimation by flame photometry.
- (v) The alkaline earth metals like those of alkali metals have high electrical and thermal conductivities which are typical characteristics of metals.

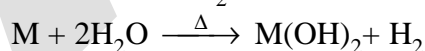
### 10.6.6 Chemical Properties

The alkaline earth metals are less reactive than the alkali metals. The reactivity of these elements increases on going down the group.

- (i) **Reactivity towards air :** Beryllium and magnesium are kinetically inert to oxygen and water because of the formation of an oxide film on their surface. However, powdered beryllium burns brilliantly on ignition in air to give  $\text{BeO}$  and  $\text{Be}_3\text{N}_2$ . Magnesium is more electropositive and burns with dazzling brilliance in air to give  $\text{MgO}$  and  $\text{Mg}_3\text{N}_2$ . Calcium, strontium and barium are readily attacked by air to form the oxide and nitride.

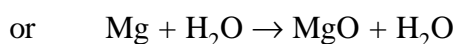
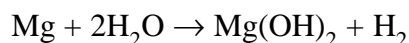
- (ii) **Reactivity towards water.**

Reaction with  $\text{H}_2\text{O}$  : AEM have lesser tendency to react with water as compared to AM. They form hydroxides and liberate  $\text{H}_2$  on reaction with  $\text{H}_2\text{O}$



\* Be is inert towards water.

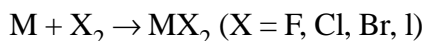
\* Magnesium react as



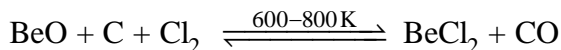
$\text{MgO}$  forms protective layer, that is why it does not react readily unless layer is removed amalgamating with Hg. Other metals react quite readily (Ca, Sr, Ba).

**Note:**  $\text{Be}(\text{OH})_2$  is amphoteric but other hydroxides are basic in nature.

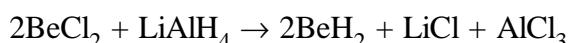
- (iii) **Reactivity towards the halogens :** All the alkaline earth metals combine with halogen at elevated temperatures forming their halides.



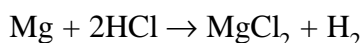
Thermal decomposition of  $(NH_4)_2BeF_4$  is the best route for the preparation of  $BeF_2$ , and  $BeCl_2$  is conveniently made from the oxide.



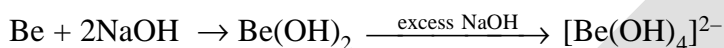
- (iv) **Reactivity towards hydrogen :** All the elements except beryllium combine with hydrogen upon heating to form their hydrides,  $MH_2$ .  $BeH_2$ , however, can be prepared by the reaction of  $BeCl_2$  with  $LiAlH_4$ .



- (v) **Reactivity towards acids :** AEM react with acids & liberate  $H_2$

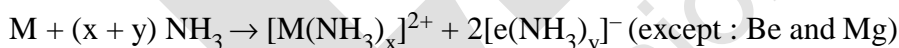


Be is amphoteric as it also react with NaOH, other metals do not react as they are purely basic.



- (vi) **Reducing nature :** Like alkali metals, the alkaline earth metals are strong reducing agents. This is indicated by large negative values of their reduction potentials. However their reducing power is less than those of their corresponding alkali metals. Beryllium has less negative value compared to other alkaline earth metals. However, its reducing nature is due to large hydration energy associated with the small size of  $Be^{2+}$  ion and relatively large value of the atomization enthalpy of the metal.

- (vii) **Solutions in liquid ammonia :** Like alkali metals, the alkaline earth metals dissolve in liquid ammonia to give deep blue black solutions forming ammoniated ions.



From these solutions, the ammoniates,  $[M(NH_3)_6]^{2+}$  can be recovered.

### 10.6.7 Uses :

**Be :** Beryllium is used in the manufacture of alloys. Copper-beryllium alloys are used in the preparation of high strength springs. Metallic beryllium is used for making windows of X-ray tubes.

**Mg :** Magnesium forms alloys with aluminium, zinc, manganese and tin. Magnesium-aluminium alloys being light in mass are used in air-craft construction. Magnesium (powder and ribbon) is used in flash powders and bulbs, incendiary bombs and signals. A suspension of magnesium hydroxide in water (called *milk of magnesia*) is used as antacid in medicine. Magnesium carbonate is an ingredient of toothpaste.

**Ca :** Calcium is used in the extraction of metals from oxides which are difficult to reduce with carbon. Calcium and barium metals, owing to their reactivity with oxygen and nitrogen at elevated temperatures, have often been used to remove air from vacuum tubes.

**Ra :** Radium salts are used in radiotherapy, for example, in the treatment of cancer.

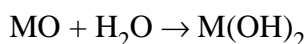


## 10.7 GENERAL CHARACTERISTICS OF COMPOUNDS OF THE ALKALINE EARTH METALS

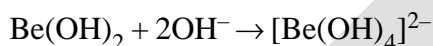
The dipositive oxidation state ( $M^{2+}$ ) is the predominant valence of Group 2 elements. The alkaline earth metals form compounds which are predominantly ionic but less ionic than the corresponding compounds of alkali metals. This is due to increased nuclear charge and smaller size. The oxides and other compounds of beryllium and magnesium are more covalent than those formed by the heavier and large sized members (Ca, Sr, Ba). The general characteristics of some of the compounds of alkali earth metals are described below.

### (i) *Oxides and Hydroxides :*

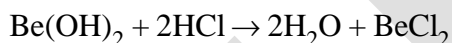
The alkaline earth metals burn in oxygen to form the monoxide, MO which, except for BeO, have rock-salt structure. The BeO is essentially covalent in nature. The enthalpies of formation of these oxides are quite high and consequently they are very stable to heat. BeO is amphoteric while oxides of other elements are ionic in nature. All these oxides except BeO are basic in nature and react with water to form sparingly soluble hydroxides.



The solubility, thermal stability and the basic character of these hydroxides increase with increasing atomic number from  $Mg(OH)_2$  to  $Ba(OH)_2$ . The alkaline earth metal hydroxides are, however, less basic and less stable than alkali metal hydroxides. Beryllium hydroxide is amphoteric in nature as it reacts with acid and alkali both.

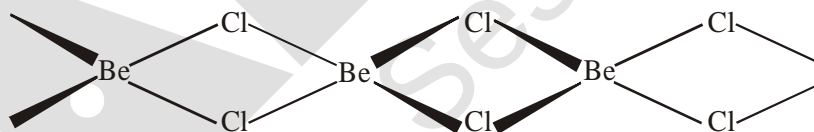


Beryllate ion



### (ii) *Halides :*

Except for beryllium halides, all other halides of alkaline earth metals are ionic in nature. Beryllium halides are essentially covalent and soluble in organic solvents. Beryllium chloride has a chain structure in the solid state as shown below:



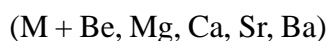
In the vapour phase  $BeCl_2$  tends to form a chloro-bridged dimer which dissociates into the linear monomer at high temperatures of the order of 1200 K. The tendency to form halide hydrates gradually decreases (for example,  $MgCl_2 \cdot 8H_2O$ ,  $CaCl_2 \cdot 6H_2O$ ,  $SrCl_2 \cdot 6H_2O$  and  $BaCl_2 \cdot 2H_2O$ ) down the group. The dehydration of hydrated chlorides, bromides and iodides of Ca, Sr and Ba can be achieved on heating; however, the corresponding hydrated halides of Be and Mg on heating suffer hydrolysis. The fluorides are relatively less soluble than the chlorides owing to their high lattice energies.

(iii) **Salts of Oxoacids** : The alkaline earth metals also form salts of oxoacids. Some of these are :

**Carbonates** : Carbonates of alkaline earth metals are insoluble in water and can be precipitated by addition of a sodium or ammonium carbonate solution to a solution of a soluble salt of these metals. The solubility of carbonates in water decreases as the atomic number of the metal ion increases. All the carbonates decompose on heating to give carbon dioxide and the oxide. Beryllium carbonate is unstable and can be kept only in the atmosphere of  $\text{CO}_2$ . The thermal stability increases with increasing cationic size.

**Sulphates** : The sulphates of the alkaline earth metals are all white solids and stable to heat.  $\text{BeSO}_4$ , and  $\text{MgSO}_4$  are readily soluble in water; the solubility decreases from  $\text{CaSO}_4$  to  $\text{BaSO}_4$ . The greater hydration enthalpies of  $\text{Be}^{2+}$  and  $\text{Mg}^{2+}$  ions overcome the lattice enthalpy factor and therefore their sulphates are soluble in water.

**Nitrates** : The nitrates are made by dissolution of the carbonates in dilute nitric acid. Magnesium nitrate crystallises with six molecules of water, whereas barium nitrate crystallises as the anhydrous salt. This again shows a decreasing tendency to form hydrates with increasing size and decreasing hydration enthalpy. All of them decompose on heating to give the oxide like lithium nitrate.



#### Problem 10.4

Why does the solubility of alkaline earth metal hydroxides in water increase down the group?

#### Solution

Among alkaline earth metal hydroxides, the anion being common the cationic radius will influence the lattice enthalpy. Since lattice enthalpy decreases much more than the hydration enthalpy with increasing ionic size, the solubility increases as we go down the group.

#### Problem 10.5

Why does the solubility of alkaline earth metal carbonates and sulphates in water decrease down the group?

#### Solution

The size of anions being much larger compared to cations, the lattice enthalpy will remain almost constant within a particular group. Since the hydration enthalpies decrease down the group, solubility will decrease as found for alkaline earth metal carbonates and sulphates.

### 10.8 ANOMALOUS BEHAVIOUR OF BERYLLIUM

Beryllium, the first member of the Group 2 metals, shows anomalous behaviour as compared to magnesium and rest of the members. Further, it shows diagonal relationship to aluminium which is discussed subsequently.

- (i) Beryllium has exceptionally small atomic and ionic sizes and thus does not compare well with other members of the group. Because of high ionisation enthalpy and small size it forms compounds which are largely covalent and get easily hydrolysed.
- (ii) Beryllium does not exhibit coordination number more than four as in its valence shell there are only four orbitals. The remaining members of the group can have a coordination number of six by making use of *d*-orbitals.
- (iii) The oxide and hydroxide of beryllium, unlike the hydroxides of other elements in the group, are amphoteric in nature.

### 10.8.1 Diagonal Relationship between Beryllium and Aluminium

The ionic radius of  $\text{Be}^{2+}$  is estimated to be 31 pm; the charge/radius ratio is nearly the same as that of the  $\text{Al}^{3+}$  ion. Hence beryllium resembles aluminium in some ways. Some of the similarities are:

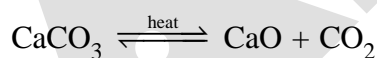
- (i) Like aluminium, beryllium is not readily attacked by acids because of the presence of an oxide film on the surface of the metal.
- (ii) Beryllium hydroxide dissolves in excess of alkali to give a beryllate ion,  $[\text{Be}(\text{OH})_4]^{2-}$  just as aluminium hydroxide gives aluminate ion,  $[\text{Al}(\text{OH})_4]^-$ .
- (iii) The chlorides of both beryllium and aluminium have  $\text{Cl}^-$  bridged chloride structure in vapour phase. Both the chlorides are soluble in organic solvents and are strong Lewis acids. They are used as Friedel Craft catalysts.
- (iv) Beryllium and aluminium ions have strong tendency to form complexes,  $\text{BeF}_4^{2-}$ ,  $\text{AlF}_6^{3-}$ .

### 10.9 SOME IMPORTANT COMPOUNDS OF CALCIUM

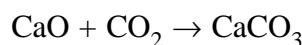
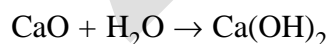
Important compounds of calcium are calcium oxide, calcium hydroxide, calcium sulphate, calcium carbonate and cement. These are industrially important compounds. The large scale preparation of these compounds and their uses are described below.

#### Calcium Oxide or Quick Lime, $\text{CaO}$

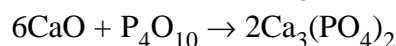
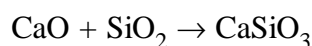
It is prepared on a commercial scale by heating limestone ( $\text{CaCO}_3$ ) in a rotary kiln at 1070-1270 K.



The carbon dioxide is removed as soon as it is produced to enable the reaction to proceed to completion. Calcium oxide is a white amorphous solid. It has a melting point of 2870 K. On exposure to atmosphere, it absorbs moisture and carbon dioxide.



The addition of limited amount of water breaks the lump of lime. This process is called *slaking of lime*. Quick lime slaked with soda gives solid sodalime. Being a basic oxide, it combines with acidic oxides at high temperature.



**Uses :** (i) It is an important primary material for manufacturing cement and is the cheapest form of alkali.

(ii) It is used in the manufacture of sodium carbonate from caustic soda.

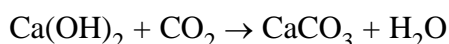
(iii) It is employed in the purification of sugar and in the manufacture of dye stuffs.

### Calcium Hydroxide (Slaked lime), $\text{Ca(OH)}_2$

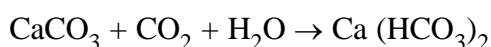
Calcium hydroxide is prepared by adding water to quick lime,  $\text{CaO}$ .

It is a white amorphous powder. It is sparingly soluble in water. The aqueous solution is known as *lime water* and a suspension of slaked lime in water is known as *milk of lime*.

When carbon dioxide is passed through lime water it turns milky due to the formation of calcium carbonate.



On passing excess of carbon dioxide, the precipitate dissolves to form calcium hydrogencarbonate.



Milk of lime reacts with chlorine to form hypochlorite, a constituent of bleaching powder.



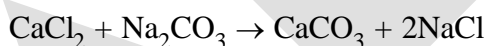
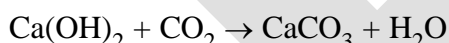
**Uses:** (i) It is used in the preparation of mortar, a building material.

(ii) It is used in white wash due to its disinfectant nature.

(iii) It is used in glass making, in tanning industry, for the preparation of bleaching powder and for purification of sugar.

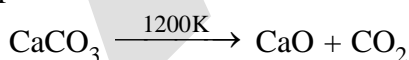
### Calcium Carbonate, $\text{CaCO}_3$

Calcium carbonate occurs in nature in several forms like limestone, chalk, marble etc. It can be prepared by passing carbon dioxide through slaked lime or by the addition of sodium carbonate to calcium chloride.

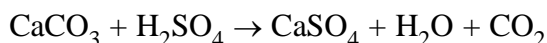
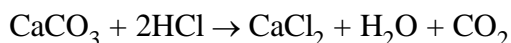


Excess of carbon dioxide should be avoided since this leads to the formation of water soluble calcium hydrogencarbonate.

Calcium carbonate is a white fluffy powder. It is almost insoluble in water. When heated to 1200 K, it decomposes to evolve carbon dioxide.



It reacts with dilute acid to liberate carbon dioxide.



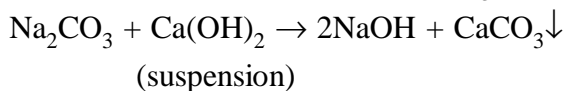
**Uses:** It is used as a building material in the form of marble and in the manufacture of quick lime. Calcium carbonate along with magnesium carbonate is used as a flux in the extraction of metals such as iron.





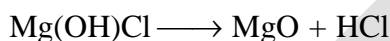
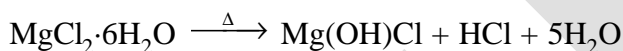
## FEW IMPORTANT POINTS

- (i) Magnesium Peroxide ( $\text{MgO}_2$ ) and Calcium Peroxide ( $\text{CaO}_2$ ) are obtained by passing  $\text{H}_2\text{O}_2$  in a suspension of  $\text{Mg}(\text{OH})_2$  and  $\text{Ca}(\text{OH})_2$ .
- (ii)  $\text{MgO}_2$  is used as an antiseptic in tooth paste and as a bleaching agent.
- (iii) Preparation of  $\text{NaOH}$  : Caustication of  $\text{Na}_2\text{CO}_3$  (Gossage's method):



Since the  $K_{\text{sp}}(\text{CaCO}_3) < K_{\text{sp}}(\text{Ca}(\text{OH})_2)$ , the reaction shifts towards right.

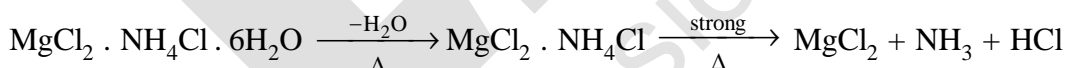
- (iv) As a reagent  $\text{KOH}$  is less frequently used but in absorption of  $\text{CO}_2$ ,  $\text{KOH}$  is preferably used compared to  $\text{NaOH}$ . Because  $\text{KHCO}_3$  formed is soluble whereas  $\text{NaHCO}_3$  is sparingly soluble and may therefore choke the tubes of apparatus used.
- (v) Calcium hydroxide is used as a mortar.  
[Mortar is a mixture of slaked lime (1 Part) and sand (3 Parts) made into paste with water.]
- (vi)  $\text{NaCl}$  is used to prepare freezing mixture in laboratory [Ice-common salt mixture is called freezing mixture and temperature goes down to  $-23^\circ\text{C}$ .]
- (vii) On heating  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  undergoes hydrolysis as follows:



\*\* Hence, Anhydrous  $\text{MgCl}_2$  cannot be prepared by heating this hydrate.

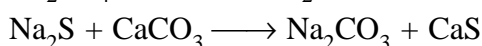
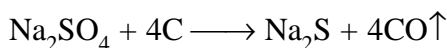
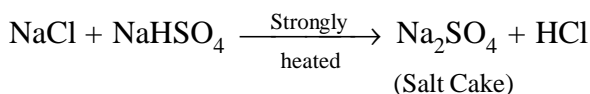
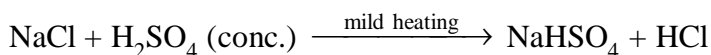
\*\* Because of the formation of  $\text{HCl}$ , sea water cannot be used in marine boilers which corrodes the iron body.

- (viii) Anhydrous  $\text{MgCl}_2$  can be prepared by heating a double salt like  $\text{MgCl}_2 \cdot \text{NH}_4\text{Cl} \cdot 6\text{H}_2\text{O}$  as follows:



- (ix) Sorel Cement is a mixture of  $\text{MgO}$  and  $\text{MgCl}_2$  (paste like) which set to hard mass on standing, this is used in dental filling, flooring etc.
- (x) Anhydrous  $\text{CaCl}_2$  is used in drying gases and organic compounds but not  $\text{NH}_3$  or alcohol due to the formation of  $\text{CaCl}_2 \cdot 8\text{NH}_3$  and  $\text{CaCl}_2 \cdot 4\text{C}_2\text{H}_5\text{OH}$ .
- (xi) One interesting feature of the solubility of Glauber's salt is; when crystallised at below  $32.4^\circ\text{C}$ , then  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  is obtained but above  $32.4^\circ\text{C}$ ,  $\text{Na}_2\text{SO}_4$  (anh.) comes out.

(xii) Leblanc Process (Preparation of  $\text{Na}_2\text{CO}_3$ ) :



## EXERCISE # O-1

SELECT THE CORRECT ALTERNATIVE (ONLY ONE CORRECT ANSWER)

## Alkali metals

- $\text{Cs}^+$  ions impart violet colour to Bunsen flame. This is due to the fact that the emitted radiations are of -  
(A) high energy (B) lower frequencies  
(C) longer wave-lengths (D) zero wave number
- The reaction of an element A with water produces combustible gas B and an aqueous solution of C. When another substance D reacts with this solution C also produces the same gas B. D also produces the same gas even on reaction with dilute  $\text{H}_2\text{SO}_4$  at room temperature. Element A imparts golden yellow colour to Bunsen flame. Then, A, B, C and D may be identified as  
(A) Na,  $\text{H}_2$ , NaOH and Zn (B) K,  $\text{H}_2$ , KOH and Zn  
(C) K,  $\text{H}_2$ , NaOH and Zn (D) Ca,  $\text{H}_2$ ,  $\text{CaCO}_3$  and Zn
- Which of the following carbonate of alkali metals has the least thermal stability?  
(A)  $\text{Li}_2\text{CO}_3$  (B)  $\text{K}_2\text{CO}_3$  (C)  $\text{Cs}_2\text{CO}_3$  (D)  $\text{Na}_2\text{CO}_3$
- The alkali metals which form normal oxide, peroxide as well as super oxides are  
(A) Na, Li (B) K, Li (C) Li, Cs (D) K, Rb
- The pair of compounds, which cannot exist together in a solution is  
(A)  $\text{NaHCO}_3$  and NaOH (B)  $\text{Na}_2\text{CO}_3$  and NaOH  
(C)  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$  (D)  $\text{NaHCO}_3$  and  $\text{H}_2\text{O}$
- Solution of sodium metal in liquid ammonia is a strong reducing agent due to presence of  
(A) solvated sodium ions (B) solvated hydrogen ions  
(C) sodium atoms or sodium hydroxide (D) solvated electrons
- The order of solubility of lithium halides in non-polar solvents follows the order  
(A)  $\text{LiI} > \text{LiBr} > \text{LiCl} > \text{LiF}$  (B)  $\text{LiF} > \text{LiI} > \text{LiBr} > \text{LiCl}$   
(C)  $\text{LiCl} > \text{LiF} > \text{LiI} > \text{LiBr}$  (D)  $\text{LiBr} > \text{LiCl} > \text{LiF} > \text{LiI}$
- The salt which finds uses in qualitative inorganic analysis is  
(A)  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  or  $\text{ZnSO}_4 \cdot 5\text{H}_2\text{O}$  (B)  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$   
(C)  $\text{Na}(\text{NH}_4)\text{HPO}_4 \cdot 4\text{H}_2\text{O}$  (D)  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$
- Fire extinguishers contain  
(A) conc.  $\text{H}_2\text{SO}_4$  solution (B)  $\text{H}_2\text{SO}_4$  and  $\text{NaHCO}_3$  solutions  
(C)  $\text{NaHCO}_3$  solution (D)  $\text{CaCO}_3$  solution
- $\text{CsBr}_3$  contains  
(A) Cs-Br covalent bonds (B)  $\text{Cs}^{3+}$  and  $\text{Br}^-$  ions  
(C)  $\text{Cs}^+$  and  $\text{Br}_3^-$  ions (D)  $\text{Cs}^{3+}$  and  $\text{Br}_3^{3-}$  ions
- $\text{Na} + \text{Al}_2\text{O}_3 \xrightarrow{\text{High temperature}} \text{X} \xrightarrow[\text{water}]{\text{CO}_2 \text{ in}} \text{Y}$ ; compound Y is  
(A)  $\text{NaAlO}_2$  (B)  $\text{NaHCO}_3$  (C)  $\text{Na}_2\text{CO}_3$  (D)  $\text{Na}_2\text{O}_2$



12. aq.  $\text{NaOH} + \text{P}_4$  (white)  $\longrightarrow \text{PH}_3 + \text{X}$ ; compound X is  
 (A)  $\text{NaH}_2\text{PO}_2$  (B)  $\text{NaHPO}_4$  (C)  $\text{Na}_2\text{CO}_3$  (D)  $\text{NaHCO}_3$
13. When  $\text{K}_2\text{O}$  is added to water, the solution becomes basic in nature because it contains a significant concentration of  
 (A)  $\text{K}^+$  (B)  $\text{O}^{2-}$  (C)  $\text{OH}^-$  (D)  $\text{O}_2^{2-}$
14. The order of melting point of chlorides of alkali metals is  
 (A)  $\text{LiCl} > \text{NaCl} > \text{KCl} < \text{CsCl}$  (B)  $\text{LiCl} > \text{NaCl} > \text{KCl} > \text{CsCl}$   
 (C)  $\text{NaCl} > \text{KCl} > \text{CsCl} > \text{LiCl}$  (D)  $\text{LiCl} > \text{NaCl} > \text{CsCl} > \text{KCl}$
15.  $\text{NaOH}(\text{Solid}) + \text{CO} \xrightarrow{200^\circ\text{C}} \text{X}$ ; product X is  
 (A)  $\text{NaHCO}_3$  (B)  $\text{Na}_2\text{CO}_3$  (C)  $\text{HCOONa}$  (D)  $\text{H}_2\text{CO}_3$
16. The aqueous solutions of lithium salts are poor conductor of electricity rather than other alkali metals because of  
 (A) high ionisation energy  
 (B) high electronegativity  
 (C) lower ability of  $\text{Li}^+$  ions to polarize water molecules  
 (D) higher degree of hydration of  $\text{Li}^+$  ions
17. In  $\text{LiAlH}_4$ , metal Al is present in  
 (A) anionic part (B) cationic part  
 (C) in both anionic and cationic part (D) neither in cationic nor in anionic part
18. Which one of the following fluoride of alkali metals has the highest lattice energy?  
 (A)  $\text{LiF}$  (B)  $\text{CsF}$  (C)  $\text{NaF}$  (D)  $\text{KF}$
19. Crown ethers and cryptands form  
 (A) complexes with alkali metals  
 (B) salts of alkali metals  
 (C) hydroxides of alkali metals used for inorganic quantitative analysis  
 (D) organic salts of alkali metals
20. The correct order of degree of hydration of  $\text{M}^+$  ions of alkali metals is  
 (A)  $\text{Li}^+ < \text{K}^+ < \text{Na}^+ < \text{Rb}^+ < \text{Cs}^+$  (B)  $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$   
 (C)  $\text{Cs}^+ < \text{Rb}^+ < \text{K}^+ < \text{Na}^+ < \text{Li}^+$  (D)  $\text{Cs}^+ < \text{Rb}^+ < \text{Na}^+ < \text{K}^+ < \text{Li}^+$
21. The commercial method of preparation of potassium by reduction of molten  $\text{KCl}$  with metallic sodium at  $850^\circ\text{C}$  is based on the fact that  
 (A) potassium is solid and sodium distils off at  $850^\circ\text{C}$   
 (B) potassium being more volatile and distils off thus shifting the reaction forward  
 (C) sodium is less reactive than potassium at  $850^\circ\text{C}$  with respect to  $\text{Cl}_2$   
 (D) sodium has less affinity to chloride ions in the presence of potassium ion

#### Alkaline earth metals

22. The 'milk of magnesia' used as an antacid is chemically  
 (A)  $\text{Mg}(\text{OH})_2$  (B)  $\text{MgO}$  (C)  $\text{MgCl}_2$  (D)  $\text{MgO} + \text{MgCl}_2$



34. A metal M readily forms water soluble sulphate, and water insoluble hydroxide  $M(OH)_2$ . Its oxide MO is amphoteric, hard and having high melting point. The alkaline earth metal M must be  
 (A) Mg (B) Be (C) Ca (D) Sr

35. (White ppt) D  $\xleftarrow{\text{Na}_2\text{CO}_3}$  A  $\xrightarrow[\text{(in acetic acid)}]{\text{K}_2\text{CrO}_4}$  B (Yellow ppt)  
 $\text{dil. H}_2\text{SO}_4 \downarrow$   
 C (White ppt)

If A is the metallic salt, then the white ppt. of D must be of

- (A) strontium carbonate (B) red lead  
 (C) barium carbonate (D) calcium carbonate

36. (Milky Cloud) C  $\xleftarrow{\text{CO}_2}$  A +  $\text{Na}_2\text{CO}_3 \longrightarrow$  B + C

The chemical formulae of A and B are

- (A) NaOH and  $\text{Ca(OH)}_2$  (B)  $\text{Ca(OH)}_2$  and NaOH  
 (C) NaOH and CaO (D) CaO and  $\text{Ca(OH)}_2$
37. The correct order of basic-strength of oxides of alkaline earth metals is  
 (A)  $\text{BeO} > \text{MgO} > \text{CaO} > \text{SrO}$   
 (B)  $\text{SrO} > \text{CaO} > \text{MgO} > \text{BeO}$   
 (C)  $\text{BeO} > \text{CaO} > \text{MgO} > \text{SrO}$   
 (D)  $\text{SrO} > \text{MgO} > \text{CaO} > \text{BeO}$

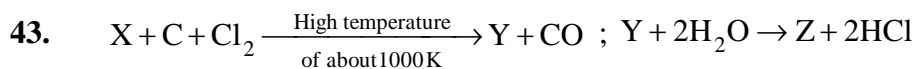
38.  $\text{X} \xrightarrow{\text{N}_2, \Delta} \text{Y} \xrightarrow{\text{H}_2\text{O}} \text{Z (colourless gas)} \xrightarrow{\text{CuSO}_4} \text{T (blue colour)}$

Then, substances Y and T are

- (A)  $\text{Y} = \text{Mg}_3\text{N}_2$  and  $\text{T} = \text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (B)  $\text{Y} = \text{Mg}_3\text{N}_2$  and  $\text{T} = \text{CuSO}_4 \cdot 4\text{NH}_3$   
 (C)  $\text{Y} = \text{Mg(NO}_3)_2$  and  $\text{T} = \text{CuO}$  (D)  $\text{Y} = \text{MgO}$  and  $\text{T} = \text{CuSO}_4 \cdot 4\text{NH}_3$
39. Weakest base among KOH, NaOH,  $\text{Ca(OH)}_2$  and  $\text{Zn(OH)}_2$  is  
 (A)  $\text{Ca(OH)}_2$  (B) KOH  
 (C) NaOH (D)  $\text{Zn(OH)}_2$
40. If X and Y are the second ionisation potentials of alkali and alkaline earth metals of same period, then -  
 (A)  $\text{X} > \text{Y}$  (B)  $\text{X} < \text{Y}$  (C)  $\text{X} = \text{Y}$  (D)  $\text{X} \ll \text{Y}$

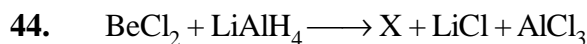
41.  $\text{X} \xrightarrow{\text{CoCl}_2} \text{CaCl}_2 + \text{Y} \uparrow$ ; the effective ingredient of X is

- (A)  $\text{OCl}^-$  (B)  $\text{Cl}^-$  (C)  $\text{OCl}^+$  (D)  $\text{OCl}_2^-$
42. White heavy precipitate is formed when  $\text{BaCl}_2$  is added to a clear solution of compound A. Precipitate is insoluble in dilute HCl. Then, the compound A is  
 (A) a bicarbonate (B) a carbonate  
 (C) a sulphate (D) a chloride



Compound Y is found in polymeric chain structure and is an electron deficient molecule. Y must be

- (A) BeO (B) BeCl<sub>2</sub> (C) BeH<sub>2</sub> (D) AlCl<sub>3</sub>



- (A) X is LiH (B) X is BeH<sub>2</sub>  
(C) X is BeCl<sub>2</sub>·2H<sub>2</sub>O (D) None

45. The order of thermal stability of carbonates of IIA group is

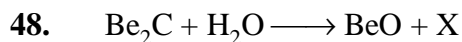
- (A) BaCO<sub>3</sub> > SrCO<sub>3</sub> > CaCO<sub>3</sub> > MgCO<sub>3</sub>  
(B) MgCO<sub>3</sub> > CaCO<sub>3</sub> > SrCO<sub>3</sub> > BaCO<sub>3</sub>  
(C) CaCO<sub>3</sub> > SrCO<sub>3</sub> > BaCO<sub>3</sub> > MgCO<sub>3</sub>  
(D) MgCO<sub>3</sub> = CaCO<sub>3</sub> > SrCO<sub>3</sub> = BaCO<sub>3</sub>

46. A pair of substances which gives all the same products on reaction with water is

- (A) Mg and MgO (B) Sr and SrO (C) Ca and CaH<sub>2</sub> (D) Be and BeO

47. A metal which is soluble in both water and liquid NH<sub>3</sub> separately -

- (A) Cr (B) Mn (C) Ba (D) Al



$CaC_2 + H_2O \longrightarrow Ca(OH)_2 + Y$ ; then X and Y are respectively

- (A) CH<sub>4</sub>, CH<sub>4</sub> (B) CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> (C) CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub> (D) C<sub>2</sub>H<sub>2</sub>, CH<sub>4</sub>

49. Which of the following groups of elements have chemical properties that are most similar

- (A) Na, K, Ca (B) Mg, Sr, Ba (C) Be, Al, Ca (D) Be, Ra, Cs

50. MgBr<sub>2</sub> and MgI<sub>2</sub> are soluble in acetone because of

- (A) Their ionic nature (B) Their coordinate nature  
(C) Their metallic nature (D) Their covalent nature

## EXERCISE # O-2

SELECT THE CORRECT ALTERNATIVES (ONE OR MORE THEN ONE CORRECT ANSWERS)

*Alkali metals*

- Nitrogen dioxide can be prepared by heating -  
(A)  $\text{KNO}_3$  (B)  $\text{AgNO}_3$  (C)  $\text{Pb}(\text{NO}_3)_2$  (D)  $\text{Cu}(\text{NO}_3)_2$
- Which of the following compounds are not paramagnetic in nature?  
(A)  $\text{KO}_2$  (B)  $\text{K}_2\text{O}_2$  (C)  $\text{Na}_2\text{O}_2$  (D)  $\text{RbO}_2$
- The golden yellow colour associated with NaCl to Bunsen flame can be explained on the basis of  
(A) low ionisation potential of sodium  
(B) emission spectrum  
(C) photosensitivity of sodium  
(D) sublimation of metallic sodium of yellow vapours
- $\text{KO}_2$  finds use in oxygen cylinders used for space and submarines. The fact(s) related to such use of  $\text{KO}_2$  is/are  
(A) it produces  $\text{O}_2$  (B) it produces  $\text{O}_3$   
(C) it absorbs  $\text{CO}_2$  (D) it absorbs both CO and  $\text{CO}_2$
- The compound(s) which have  $-\text{O}-\text{O}-$  bond(s) is/are  
(A)  $\text{BaO}_2$  (B)  $\text{Na}_2\text{O}_2$  (C)  $\text{CrO}_5$  (D)  $\text{Fe}_2\text{O}_3$
- Highly pure dilute solution of sodium in ammonia  
(A) shows blue colouration due to solvated electrons  
(B) shows electrical conductivity due to both solvated electrons as well as solvated sodium ions  
(C) shows red colouration due to solvated electrons but a bad conductor of electricity  
(D) produces hydrogen gas or carbonate
- Sodium metal is highly reactive and can be stored under  
(A) toluene (B) kerosene oil (C) alcohol (D) benzene

*Alkaline earth metals*

- The compound(s) of II<sup>nd</sup> A metals, which are amphoteric in nature is/are  
(A) BeO (B) MgO (C)  $\text{Be}(\text{OH})_2$  (D)  $\text{Mg}(\text{OH})_2$
- The correct statement is/are  
(A)  $\text{BeCl}_2$  is a covalent compound (B)  $\text{BeCl}_2$  is an electron deficient molecule  
(C)  $\text{BeCl}_2$  can form dimer (D) the hybrid state of Be in  $\text{BeCl}_2$  is  $\text{sp}^2$
- Which of the following substance(s) is/are used in laboratory for drying purposes?  
(A) anhydrous  $\text{P}_2\text{O}_5$  (B) graphite  
(C) anhydrous  $\text{CaCl}_2$  (D)  $\text{Na}_3\text{PO}_4$
- $\text{Na}_2\text{SO}_4$  is water soluble but  $\text{BaSO}_4$  is insoluble because  
(A) the hydration energy of  $\text{Na}_2\text{SO}_4$  is higher than that of its lattice energy  
(B) the hydration energy of  $\text{Na}_2\text{SO}_4$  is less than that of its lattice energy  
(C) the hydration energy of  $\text{BaSO}_4$  is less than that of its lattice energy  
(D) the hydration energy of  $\text{BaSO}_4$  is higher than that of its lattice energy

12. Which of the following statements are false?
- (A)  $\text{BeCl}_2$  is a linear molecule in the vapour state but it is polymeric form in the solid state  
 (B) Calcium hydride is called hydrolith.  
 (C) Carbides of both Be and Ca react with water to form acetylene  
 (D) Oxides of both Be and Ca are amphoteric.
13. Which of the following are ionic carbides?
- (A)  $\text{CaC}_2$                       (B)  $\text{Al}_4\text{C}_3$                       (C)  $\text{SiC}$                       (D)  $\text{Be}_2\text{C}$
14. Which of the following orders are **CORRECT** :
- (A)  $\text{AgCl} > \text{AgF}$  : Covalent character order  
 (B)  $\text{BaO} > \text{BaF}_2$  : Melting point order  
 (C)  $\text{BeF}_2 > \text{BaF}_2$  : Solubility order  
 (D)  $\text{LiNO}_3 < \text{RbNO}_3$  : Thermal stability order
15. Which of the following statements are **CORRECT** :
- (A) Mg is present in chlorophyll  
 (B) Alkaline earth metals does not form super oxide  
 (C)  $\text{NaHCO}_3$  is known as baking soda  
 (D) Permanent hardness of water is removed by boiling
16. Which of the following carbides on hydrolysis does not form methane :
- (A)  $\text{Be}_2\text{C}$                       (B)  $\text{CaC}_2$                       (C)  $\text{SrC}_2$                       (D)  $\text{Mg}_2\text{C}_3$
17. Select the incorrect order for given properties :
- (A) Thermal stability :  $\text{BaSO}_4 > \text{SrSO}_4 > \text{CaSO}_4$   
 (B) Solubility :  $\text{BaSO}_4 > \text{SrSO}_4 > \text{CaSO}_4$   
 (C) Thermal stability :  $\text{Li}_2\text{CO}_3 < \text{Na}_2\text{CO}_3 < \text{K}_2\text{CO}_3$   
 (D) Solubility :  $\text{Li}_2\text{CO}_3 > \text{Na}_2\text{CO}_3 > \text{K}_2\text{CO}_3$
18. The correct statement(s) is/are
- (A) Mg cannot form complexes  
 (B) Be can form complexes due to a very small atomic size  
 (C) the first ionisation potential of Be is higher than that of Mg  
 (D) Mg forms an alkaline hydroxide while Be forms amphoteric oxides
19. Which of the following is are the characteristic of barium?
- (A) It produce water soluble sulphide, sulphite and sulphate  
 (B) It is a silvery white metal  
 (C) It forms  $\text{Ba}(\text{NO}_3)_2$  which is used in preparation of green fire  
 (D) It produce blue-black solution in liquid ammonia

## EXERCISE # S-1

## NUMERIC GRID TYPE QUESTIONS :

1. Find the number of compounds from the following in which the element in the anionic part is in the minimum oxidation state of it



2. How many nitrate groups are present in 1 molecule of Basic beryllium nitrate?

3. Consider the following order :

(1)  $\text{CH}_4 < \text{CCl}_4 < \text{CF}_4$  : E.N. of central atom C

(2)  $\text{Mg}^{+2} < \text{K}^+ < \text{S}^{-2} < \text{Se}^{-2}$  : Ionic radius

(3)  $\text{Be}_{(\text{aq})}^{+2} > \text{Mg}_{(\text{aq})}^{+2} > \text{Ca}_{(\text{aq})}^{+2}$  : Ionic mobility

(4)  $\text{Be}^{+2} > \text{Li}^+ > \text{Al}^{+3}$  : Hydrated size

(5)  $\text{Be} > \text{Li} > \text{Cs}$  : Reducing power

(6)  $\text{F}_{(\text{aq})}^{\ominus} > \text{Cl}_{(\text{aq})}^{\ominus} > \text{Br}_{(\text{aq})}^{\ominus}$  : Electrical conductance in infinite dilute solution

Then calculate value of  $|x - y|^2$ , where x and y are correct and incorrect orders respectively.

4. Consider the following elements :

Li, Cs, Mg, Pb, Al, N

- $x$  = number of elements which can form MO type of oxides.
- $y$  = the highest oxidation state shown by any one of them.
- $z$  = the number of elements which can form amphoteric oxide(s).

Find the sum of  $x$ ,  $y$  and  $z$ .

**Fill your answer as sum of digits till you get the single digit answer.**

5. Find the number of s-block elements which can produce ammoniated cation and ammoniated electron with liquid ammonia.

Li, Na, K, Rb, Cs, Ca, Sr, Ba

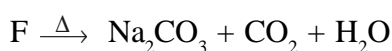
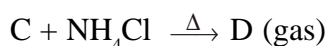
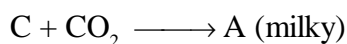
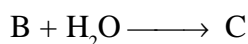
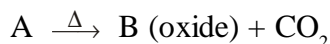
6. How many of the following metal chlorides impart characteristic colour to the oxidising flame.

$\text{LiCl}$ ,  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{BeCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{SrCl}_2$ ,  $\text{BaCl}_2$

## EXERCISE # S-2

## COMPREHENSION BASED QUESTIONS

## Comprehension # 1



- A is :  
 (A)  $\text{Ca}(\text{HCO}_3)_2$       (B)  $\text{CaCO}_3$       (C)  $\text{CaO}$       (D)  $\text{Na}_2\text{CO}_3$
- B and C are :  
 (A)  $\text{CaO}$ ,  $\text{Ca}(\text{OH})_2$       (B)  $\text{Ca}(\text{OH})_2$ ,  $\text{CaCO}_3$   
 (C)  $\text{CaCO}_3$ ,  $\text{Ca}(\text{OH})_2$       (D)  $\text{Ca}(\text{OH})_2$ ,  $\text{CaO}$
- D, E and F are :  
 (A)  $\text{NH}_3$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{HCO}_3$       (B)  $\text{NH}_3$ ,  $\text{NH}_4\text{HCO}_3$ ,  $\text{NaHCO}_3$   
 (C)  $\text{NH}_4\text{HCO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$       (D) None

## Comprehension # 2

Alkali metals readily react with oxyacids forming corresponding salts like  $\text{M}_2\text{CO}_3$ ,  $\text{MHCO}_3$ ,  $\text{MNO}_3$ ,  $\text{M}_2\text{SO}_4$  etc. with evolution of hydrogen. They also dissolve in liquid  $\text{NH}_3$  but without the evolution of hydrogen. The colour of its dilute solution is blue but when it is heated and concentrated then its colour becomes bronze.

- Among the nitrate of alkali metals which one can be decomposed to its oxide easily?  
 (A)  $\text{NaNO}_3$       (B)  $\text{KNO}_3$       (C)  $\text{LiNO}_3$       (D)  $\text{RbNO}_3$
- Among the carbonates of alkali metals which one has highest stability?  
 (A)  $\text{Cs}_2\text{CO}_3$       (B)  $\text{Rb}_2\text{CO}_3$       (C)  $\text{K}_2\text{CO}_3$       (D)  $\text{Na}_2\text{CO}_3$
- Which of the following statement about the sulphate of alkali metal is correct?  
 (A) Except  $\text{Li}_2\text{SO}_4$  all sulphate of other alkali metals are soluble in water  
 (B) All sulphates of alkali metals except lithium sulphate forms alum.  
 (C) The sulphates of alkali metals cannot be hydrolysed.  
 (D) All of these



7. Which of the following statement about solution of alkali metals in liquid ammonia is correct?
- (A) The solution have strong oxidizing properties.  
 (B) Both the dilute solution as well as concentrated solution are paramagnetic in nature  
 (C) Charge transfer is the responsible for the colour of the solution  
 (D) None of these
8. Which metal bicarbonates does not exist in solid state?
- (i)  $\text{LiHCO}_3$                       (ii)  $\text{Ca}(\text{HCO}_3)_2$                       (iii)  $\text{Zn}(\text{HCO}_3)_2$   
 (iv)  $\text{NaHCO}_3$                       (v)  $\text{AgHCO}_3$
- (A) (i), (ii), (iii), (v)      (B) (i), (ii), (iii)      (C) (i), (ii), (v)      (D) (ii), (iii), (iv)

**MATCH THE COLUMN :****9. Column-I**

- (A) Hydrolith  
 (B) Nitrolim  
 (C) Dolomite  
 (D) Pearl's ash

**Column-II**

- (P) Contain Ca  
 (Q) Used as a fertilizer  
 (R) Used to prepare  $\text{H}_2$   
 (S) Contain potassium

**10. Column-I**

- (A) Metal sulphate  $\xrightarrow{\Delta}$  metal oxide +  $\text{SO}_2$  +  $\text{O}_2$   
 (B) Metal cation +  $\text{K}_2\text{CrO}_4 \longrightarrow$  yellow ppt  
 (C) Metal +  $\text{NH}_3 \xrightarrow{\text{(liquid)}}$  blue solution  
 (D)  $\text{MCl}_2 + \text{conc. H}_2\text{SO}_4 \longrightarrow$  white ppt.

**Column-II**

- (P) Ba  
 (Q) Sr  
 (R) Na  
 (S) Mg

**MATCH THE CODE :****11. List-I**

- (P)  $\text{CaH}_2$   
 (Q)  $\text{K}_2\text{O}_2$   
 (R)  $\text{KO}_2$   
 (S)  $\text{NaCl}$

**List-II**

- (1) Paramagnetic anion  
 (2) Homodiatomic, diamagnetic anion  
 (3) Neutral aqueous solution  
 (4) Gives hydrogen on hydrolysis

**Codes :**

|     | P | Q | R | S |
|-----|---|---|---|---|
| (A) | 3 | 2 | 1 | 4 |
| (B) | 4 | 2 | 3 | 1 |
| (C) | 4 | 3 | 2 | 1 |
| (D) | 4 | 2 | 1 | 3 |

| 12. | Column-I                                     | Column-II                    |
|-----|----------------------------------------------|------------------------------|
|     | (P) Solvay process used for                  | (1) NaCl                     |
|     | (Q) Evolve $\text{CO}_2 \uparrow$ on heating | (2) $\text{Na}_2\text{O}_2$  |
|     | (R) aq. soln. is neutral towards litmus      | (3) $\text{NaHCO}_3$         |
|     | (S) Oxone                                    | (4) $\text{Na}_2\text{CO}_3$ |

Codes :

|     | P   | Q | R | S |
|-----|-----|---|---|---|
| (A) | 3,4 | 3 | 1 | 2 |
| (B) | 4,1 | 1 | 3 | 2 |
| (C) | 2,3 | 4 | 1 | 3 |
| (D) | 2,4 | 1 | 3 | 4 |

### ASSERTION & REASONING :

Questions given below consist of two statements each printed as Assertion (A) and Reason (R); while answering these questions you are required to choose any one of the following four responses:

- (A) if both (A) and (R) are true and (R) is the correct explanation of (A)
- (B) if both (A) and (R) are true but (R) is not correct explanation of (A)
- (C) if (A) is true but (R) is false
- (D) if (A) is false and (R) is true

13. **Assertion :** Beryllium does not impart any characteristic colour to the bunsen flame.  
**Reason :** Due to its very high ionization energy, beryllium requires a large amount of energy for excitation of the electrons.
14. **Assertion :** In fused state, calcium chloride cannot be used to dry alcohol or  $\text{NH}_3$ .  
**Reason :** Anhyd.  $\text{CaCl}_2$  is not a good desiccant.
15. **Assertion :** Diagonal relationship is shown between Be and Al.  
**Reason :** Ionic potential of Be is almost the same as that of Al.
16. **Assertion :** Beryllium halides dissolve in organic solvents.  
**Reason :** Beryllium halides are ionic in character.
17. **Assertion :**  $\text{BeCl}_2$  fumes in moist air.  
**Reason :**  $\text{BeCl}_2$  reacts with moisture to form HCl gas.
18. **Assertion :** Calcium carbide on hydrolysis gives methane.  
**Reason :** Calcium carbide contains  $\text{C}_2^{2-}$  anion.
19. **Assertion :** When  $\text{CO}_2$  is passed through lime water, it first turns milky and then the solution becomes clear when the passage of  $\text{CO}_2$  is continued.  
**Reason :** The milkiness is due to the formation of insoluble  $\text{CaCO}_3$  which then changes to soluble  $\text{Ca}(\text{HCO}_3)_2$  when excess of  $\text{CO}_2$  is present.
20. **Assertion :**  $\text{MgCO}_3$  is soluble in water when a current of  $\text{CO}_2$  is passed.  
**Reason :** The solubility of  $\text{MgCO}_3$  is due to the formation of  $\text{Mg}(\text{HCO}_3)_2$ .

**MATCHING LIST TYPE 1 × 3 Q. (THREE LIST TYPE Q.)**

The following column 1, 2, 3 represent elements of s block and their different oxide formation abilities.

Answer the questions that follow

**Column-1 - Elements of s-Block**

**Column-2 - Product formed on reaction with excess oxygen**

**Column-3 - Characteristics of species form on reaction with excess oxygen**

| Column - 1<br>Elements | Column - 2<br>Product formed on reaction<br>with excess oxygen | Column - 3<br>Characteristics of species form<br>on reaction with excess oxygen |
|------------------------|----------------------------------------------------------------|---------------------------------------------------------------------------------|
| (I) Na                 | (A) Superoxide                                                 | (P) Paramagnetic                                                                |
| (II) Ba                | (B) Peroxide                                                   | (Q) Diamagnetic                                                                 |
| (III) K                | (C) Monooxide                                                  | (R) Bond order = 1.5                                                            |
| (IV) Ca                | (D) Dioxide                                                    | (S) Bond order = 1                                                              |

21. Which of the following is an **INCORRECT** match.  
 (A) (I), (B), (QS)      (B) (II), (B), (QS)      (C) (II), (A), (PR)      (D) (IV), (C), (Q)
22. Which of the following matches will result in species having magnetic moment equal to that of  $\text{Mn}^{+6}$   
 (A) I, (B), QS      (B) IV, B, (QS)      (C) IV, (A), (PR)      (D) III, (A), (PR)
23. On reaction with oxygen, which of the following combination is possible  
 (A) I, (A, C), (P, Q)      (B) I, (B), (Q)  
 (C) II, (A, B), (P, Q, S)      (D) IV, (B, C), Q

## EXERCISE # JEE-MAIN

1. A metal M readily forms its sulphate  $\text{MSO}_4$  which is water soluble. It forms oxide MO which becomes inert on heating. It forms insoluble hydroxide which is soluble in NaOH. The metal M is:- [AIEEE-2002]  
 (1) Mg (2) Ba (3) Ca (4) Be
2.  $\text{KO}_2$  is used in space and submarines because it [AIEEE-2002]  
 (1) Absorbs  $\text{CO}_2$  and increase  $\text{O}_2$  concentration  
 (2) Absorbs moisture  
 (3) Absorbs  $\text{CO}_2$   
 (4) Produces ozone
3. In curing cement plasters, water is sprinkled from time to time. This helps in :- [AIEEE-2003]  
 (1) Hydrating sand and gravel mixed with cement  
 (2) Converting sand into silicate  
 (3) Developing interlocking needle like crystals of hydrated silicates  
 (4) Keeping it cool
4. The solubilities of carbonates decreases down the magnesium group due to decrease in-[AIEEE-2003]  
 (1) Inter-ionic attraction  
 (2) Entropy of solution formation  
 (3) Lattice energy of solids  
 (4) Hydration energy of cations
5. The substance not likely to contain  $\text{CaCO}_3$  is :- [AIEEE-2003]  
 (1) Sea shells (2) Dolomite  
 (3) A marble statue (4) Calcined gypsum
6. One mole of magnesium nitride on reaction with excess of water gives :- [AIEEE-2004]  
 (1) Two mole of  $\text{HNO}_3$  (2) Two mole of  $\text{NH}_3$   
 (3) 1 mole of  $\text{NH}_3$  (4) 1 mole of  $\text{HNO}_3$
7. Beryllium and aluminium exhibit many properties which are similar. But the two elements differ in - [AIEEE-2004]  
 (1) Exhibiting maximum covalency in compounds  
 (2) Forming polymeric hydrides  
 (3) Forming covalent halides  
 (4) Exhibiting amphoteric nature in their oxides.
8. The ionic mobility of alkali metal ions in aqueous solution is maximum for :- [AIEEE-2006]  
 (1)  $\text{Rb}^+$  (2)  $\text{Li}^+$  (3)  $\text{Na}^+$  (4)  $\text{K}^+$
9. The products obtained on heating  $\text{LiNO}_3$  will be :- [AIEEE-2011]  
 (1)  $\text{LiNO}_2 + \text{O}_2$  (2)  $\text{Li}_2\text{O} + \text{NO}_2 + \text{O}_2$   
 (3)  $\text{Li}_3\text{N} + \text{O}_2$  (4)  $\text{Li}_2\text{O} + \text{NO} + \text{O}_2$

10. What is the best description of the change that occurs when  $\text{Na}_2\text{O(s)}$  is dissolved in water ? [AIEEE-2011]
- (1) Oxidation number of sodium decreases  
(2) Oxide ion accepts sharing in a pair of electrons  
(3) Oxide ion donates a pair of electrons  
(4) Oxidation number of oxygen increases
11. Which of the following on thermal-decomposition yields a basic as well as an acidic oxide ? [AIEEE-2012]
- (1)  $\text{NH}_4\text{NO}_3$       (2)  $\text{NaNO}_3$       (3)  $\text{KClO}_3$       (4)  $\text{CaCO}_3$
12. Fire extinguishers contain  $\text{H}_2\text{SO}_4$  and which one of the following :- [JEE MAIN-2012, Online]
- (1)  $\text{CaCO}_3$       (2)  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$   
(3)  $\text{Na}_2\text{CO}_3$       (4)  $\text{NaHCO}_3$
13. Based on lattice energy and other considerations, which one of the following alkali metal chloride is expected to have the highest melting point ? [JEE MAIN-2012, Online]
- (1)  $\text{RbCl}$       (2)  $\text{LiCl}$       (3)  $\text{KCl}$       (4)  $\text{NaCl}$
14. Which one of the following will react most vigorously with water ? [JEE MAIN-2012, Online]
- (1)  $\text{Li}$       (2)  $\text{K}$       (3)  $\text{Rb}$       (4)  $\text{Na}$
15. A metal  $\text{M}$  on heating in nitrogen gas gives  $\text{Y}$ .  $\text{Y}$  on treatment with  $\text{H}_2\text{O}$  gives a colourless gas which when passed through  $\text{CuSO}_4$  solution gives a blue colour,  $\text{Y}$  is :- [JEE MAIN-2012, Online]
- (1)  $\text{NH}_3$       (2)  $\text{MgO}$       (3)  $\text{Mg}_3\text{N}_2$       (4)  $\text{Mg}(\text{NO}_3)_2$
16. The correct statement for the molecule,  $\text{CsI}_3$ , is : [JEE(Main)-2014]
- (1) it contains  $\text{Cs}^{3+}$  and  $\text{I}^-$  ions  
(2) it contains  $\text{Cs}^+$ ,  $\text{I}^-$  and lattice  $\text{I}_2$  molecule  
(3) it is a covalent molecule  
(4) it contains  $\text{Cs}^+$  and  $\text{I}_3^-$  ions
17. Which of the following statements about  $\text{Na}_2\text{O}_2$  is **not** correct ? [JEE MAIN-2014, Online]
- (1)  $\text{Na}_2\text{O}_2$  oxidises  $\text{Cr}^{3+}$  to  $\text{CrO}_4^{2-}$  in acid medium  
(2) It is diamagnetic in nature  
(3) It is the super oxide of sodium  
(4) It is a derivative of  $\text{H}_2\text{O}_2$
18. Amongst  $\text{LiCl}$ ,  $\text{RbCl}$ ,  $\text{BeCl}_2$  and  $\text{MgCl}_2$  the compounds with the greatest and the least ionic character, respectively are : [JEE MAIN-2014, Online]
- (1)  $\text{RbCl}$  and  $\text{MgCl}_2$       (2)  $\text{LiCl}$  and  $\text{RbCl}$   
(3)  $\text{MgCl}_2$  and  $\text{BeCl}_2$       (4)  $\text{RbCl}$  and  $\text{BeCl}_2$

19. The correct order of thermal stability of hydroxides is : JEE(Main)Online-2015]  
 (1)  $\text{Ba}(\text{OH})_2 < \text{Sr}(\text{OH})_2 < \text{Ca}(\text{OH})_2 < \text{Mg}(\text{OH})_2$  (2)  $\text{Mg}(\text{OH})_2 < \text{Sr}(\text{OH})_2 < \text{Ca}(\text{OH})_2 < \text{Ba}(\text{OH})_2$   
 (3)  $\text{Mg}(\text{OH})_2 < \text{Ca}(\text{OH})_2 < \text{Sr}(\text{OH})_2 < \text{Ba}(\text{OH})_2$  (4)  $\text{Ba}(\text{OH})_2 < \text{Ca}(\text{OH})_2 < \text{Sr}(\text{OH})_2 < \text{Mg}(\text{OH})_2$
20. Which of the alkaline earth metal halides given below is essentially covalent in nature :-  
 (1)  $\text{SrCl}_2$  (2)  $\text{CaCl}_2$  (3)  $\text{BeCl}_2$  (4)  $\text{MgCl}_2$   
JEE(Main)Online-2015]
21. Which one of the following alkaline earth metal sulphates has its hydration enthalpy greater than its lattice enthalpy ? [JEE(Main)-2015]  
 (1)  $\text{BaSO}_4$  (2)  $\text{SrSO}_4$  (3)  $\text{CaSO}_4$  (4)  $\text{BeSO}_4$
22. The commercial name for calcium oxide is : [JEE(Main)-2016]  
 (1) Quick lime (2) Milk of lime (3) Limestone (4) Slaked lime
23. The correct order of the solubility of alkaline-earth metal sulphates in water is : [JEE(Main)-2016]  
 (1)  $\text{Mg} < \text{Sr} < \text{Ca} < \text{Ba}$  (2)  $\text{Mg} < \text{Ca} < \text{Sr} < \text{Ba}$   
 (3)  $\text{Mg} > \text{Ca} > \text{Sr} > \text{Ba}$  (4)  $\text{Mg} > \text{Sr} > \text{Ca} > \text{Ba}$
24. The main oxides formed on combustion of Li, Na and K in excess of air are respectively : [JEE(Main)-2016]  
 (1)  $\text{Li}_2\text{O}$ ,  $\text{Na}_2\text{O}_2$  and  $\text{KO}_2$  (2)  $\text{Li}_2\text{O}$ ,  $\text{Na}_2\text{O}$  and  $\text{KO}_2$   
 (3)  $\text{LiO}_2$ ,  $\text{Na}_2\text{O}_2$  and  $\text{K}_2\text{O}$  (4)  $\text{Li}_2\text{O}_2$ ,  $\text{Na}_2\text{O}_2$  and  $\text{KO}_2$
25. Both lithium and magnesium display several similar properties due to the diagonal relationship ; however, the one which is incorrect is : [JEE(Main)-2017]  
 (1) Both form basic carbonates  
 (2) Both form soluble bicarbonates  
 (3) Both form nitrides  
 (4) Nitrates of both Li and Mg yield  $\text{NO}_2$  and  $\text{O}_2$  on heating
26. Which of the following ions does **not** liberate hydrogen gas on reaction with dilute acids? [JEE(Main)-2017 on line]  
 (1)  $\text{Ti}^{2+}$  (2)  $\text{Cr}^{2+}$   
 (3)  $\text{Mn}^{2+}$  (4)  $\text{V}^{2+}$
27. In  $\text{KO}_2$ , the nature of oxygen species and the oxidation state of oxygen atom are, respectively [JEE(Main)ONLINE-2018]  
 (1) Superoxide and  $-1/2$   
 (2) Oxide and  $-2$   
 (3) Peroxide and  $-1/2$   
 (4) Superoxide and  $-1$



# ANSWER KEY

## EXERCISE # O-1

- |         |         |         |         |
|---------|---------|---------|---------|
| 1. (A)  | 2. (A)  | 3. (A)  | 4. (D)  |
| 5. (A)  | 6. (D)  | 7. (A)  | 8. (C)  |
| 9. (B)  | 10. (C) | 11. (C) | 12. (A) |
| 13. (C) | 14. (C) | 15. (C) | 16. (D) |
| 17. (A) | 18. (A) | 19. (A) | 20. (C) |
| 21. (B) | 22. (A) | 23. (C) | 24. (D) |
| 25. (B) | 26. (C) | 27. (B) | 28. (A) |
| 29. (C) | 30. (D) | 31. (A) | 32. (A) |
| 33. (A) | 34. (B) | 35. (C) | 36. (B) |
| 37. (B) | 38. (B) | 39. (D) | 40. (A) |
| 41. (A) | 42. (C) | 43. (B) | 44. (B) |
| 45. (A) | 46. (C) | 47. (C) | 48. (C) |
| 49. (B) | 50. (D) |         |         |

## EXERCISE # O-2

- |                 |                     |                 |                 |
|-----------------|---------------------|-----------------|-----------------|
| 1. (B),(C), (D) | 2. (B),(C)          | 3. (A),(B)      | 4. (A),(C)      |
| 5. (A),(B),(C)  | 6. (A), (B)         | 7. (A), (B),(D) | 8. (A),(C)      |
| 9. (A),(B),(C)  | 10. (A),(C)         | 11. (A), (C)    | 12. (C),(D)     |
| 13. (A),(B),(D) | 14. (A),(B),(C),(D) | 15. (A),(B),(C) | 16. (B),(C),(D) |
| 17. (B), (D)    | 18. (B),(C),(D)     | 19. (B),(C),(D) |                 |

## EXERCISE # S-1

- |        |        |        |                    |
|--------|--------|--------|--------------------|
| 1. (4) | 2. (6) | 3. (4) | 4. (10), OMR - (1) |
| 5. (8) |        |        |                    |
| 6. (6) |        |        |                    |

Except Be & Mg other s-block metals impart characteristic colour to oxidising flame.



## EXERCISE # S-2

- Comprehension Based Questions

## Comprehension # 1

1. (B)                      2. (A)                      3. (B)

## Comprehension # 2

4. (C)                      5. (A)                      6. (D)                      7. (D)                      8. (A)

- Match the column

9. (A)  $\rightarrow$  P,R ; (B)  $\rightarrow$  P,Q ; (C)  $\rightarrow$  P ; (D)  $\rightarrow$  S

10. (A)  $\rightarrow$  P,Q,S ; (B)  $\rightarrow$  P,Q ; (C)  $\rightarrow$  P,Q,R ; (D)  $\rightarrow$  P,Q

- Match the code

11. (D)                      12. (A)

- Assertion & Reasoning

13. A                      14. C                      15. A                      16. C  
 17. A                      18. D                      19. A                      20. A  
 21. C                      22. D                      23. B

## EXERCISE # JEE-MAIN

1. (4)                      2. (1)                      3. (3)                      4. (4)  
 5. (4)                      6. (2)                      7. (1)                      8. (1)  
 9. (2)                      10. (3)                      11. (4)                      12. (4)  
 13. (4)                      14. (3)                      15. (3)                      16. (4)  
 17. (3)                      18. (4)                      19. (3)                      20. (3)  
 21. (4)                      22. (1)                      23. (3)                      24. (1)  
 25. (1)                      26. (3)                      27. (1)

## EXERCISE # JEE-ADVANCED

1. A                      2. A                      3. B                      4. B  
 5. A,B                      6. B                      7. B                      8. A,B

# d-BLOCK COMPOUNDS

## TRANSITION ELEMENTS

**Definition :** They are often called 'transition elements' because their position in the periodic table is between s-block and p-block elements

Typically, the transition elements have incompletely filled d-level. Since Zn group has  $d^{10}$  configuration in their ground state as well as in stable oxidation state, they are not considered as transition elements but they are d-block elements.

| 1st Series |    |    |    |    |    |    |    |    |    |    |
|------------|----|----|----|----|----|----|----|----|----|----|
|            | Sc | Ti | V  | Cr | Mn | Fe | Co | Ni | Cu | Zn |
| Z          | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 |
| 4s         | 2  | 2  | 2  | 1  | 2  | 2  | 2  | 2  | 1  | 2  |
| 3d         | 1  | 2  | 3  | 5  | 5  | 6  | 7  | 8  | 10 | 10 |

| 2nd Series |    |    |    |    |    |    |    |    |    |    |
|------------|----|----|----|----|----|----|----|----|----|----|
|            | Y  | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd |
| Z          | 39 | 40 | 41 | 42 | 43 | 44 | 45 | 46 | 47 | 48 |
| 5s         | 2  | 2  | 1  | 1  | 2  | 1  | 1  | 0  | 1  | 2  |
| 4d         | 1  | 2  | 4  | 5  | 5  | 7  | 8  | 10 | 10 | 10 |

| 3rd Series |    |    |    |    |    |    |    |    |    |    |
|------------|----|----|----|----|----|----|----|----|----|----|
|            | La | Hf | Ta | W  | Re | Os | Ir | Pt | Au | Hg |
| Z          | 57 | 72 | 73 | 74 | 75 | 76 | 77 | 78 | 79 | 80 |
| 6s         | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 1  | 1  | 2  |
| 5d         | 1  | 2  | 3  | 4  | 5  | 6  | 7  | 9  | 10 | 10 |

| 4th Series |    |     |     |     |     |     |     |     |     |     |
|------------|----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
|            | Ac | Rf  | Db  | Sg  | Bh  | Hs  | Mt  | Ds  | Rg  | Uub |
| Z          | 89 | 104 | 105 | 106 | 107 | 108 | 109 | 110 | 111 | 112 |
| 7s         | 2  | 2   | 2   | 2   | 2   | 2   | 2   | 2   | 1   | 2   |
| 6d         | 1  | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 10  | 10  |

## General Characteristics :

(i) **Metallic character :** They are all metal and good conductor of heat & electricity

(ii) **Electronic configuration :**  $(n-1)d^{1-10}ns^{1-2}$

|            |    |    |                 |                 |    |    |    |                  |                 |    |
|------------|----|----|-----------------|-----------------|----|----|----|------------------|-----------------|----|
|            | Sc | Ti | V               | Cr              | Mn | Fe | Co | Ni               | Cu              | Zn |
| others are |    |    |                 | 4s <sup>1</sup> |    |    |    |                  | 4s <sup>1</sup> |    |
| as usual   |    |    | 3d <sup>5</sup> |                 |    |    |    | 3d <sup>10</sup> |                 |    |

(iii) **M.P.** Cr }  $\longrightarrow$  Maximum  
 Mo } 6 no. of unpaired e<sup>-</sup>  
 W } are involved in metallic bonding Hg } lowest m.p.  
 Cd } due to no unpaired e<sup>-</sup>  
 for metallic bonding

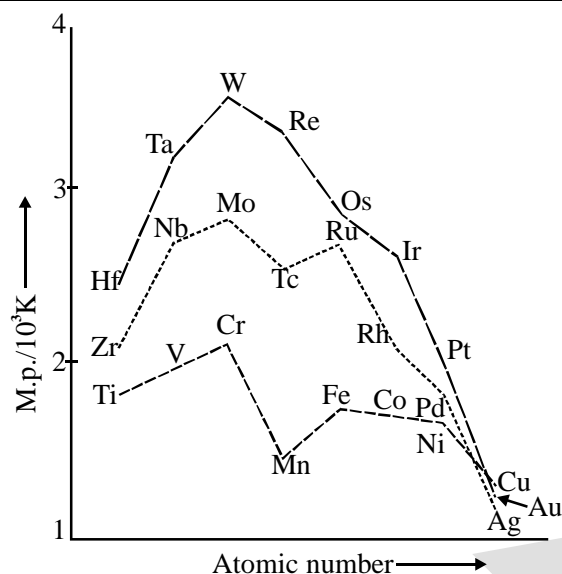


Fig. : Trends in melting points of transition elements

## (iv) Variation in atomic radius :

Sc  $\longrightarrow$  Mn Fe Co Ni Cu Zn

decreases

remains

increases

same again

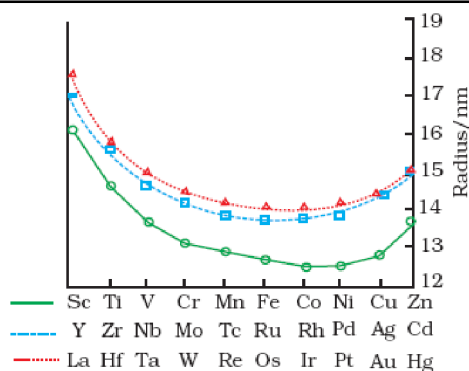


Fig. 8.3: Trends in atomic radii of transition elements

## (v) Ionisation energy :

1<sup>st</sup>, 2<sup>nd</sup>, 3<sup>rd</sup> IE's are increasing from left to right for 1<sup>st</sup> Transition series, but not regularly.

For 2<sup>nd</sup> IE Cr > Fe > Mn and Cu > Zn

For 3<sup>rd</sup> IE Mn > Cr > Fe and Zn has highest.

## (vi) DENSITY

- The atomic volume of the transition elements are low, compared with s-block, so their density is comparatively high ( $D = M/V$ )
- Os ( $22.57 \text{ gm cm}^{-3}$ ) and Ir ( $22.61 \text{ gm cm}^{-3}$ ) have highest density.
- In all the groups (except IIIB) there is normal increase in density from 3d to 4d series, and from 4d to 5d, it increases just double. Due to lanthanide contraction **Ex.** : Ti < Zr << Hf

(d) **In 3d series**

|                                  | Sc   | Ti  | V    | Cr   | Mn   | Fe  | Co  | Ni  | Cu  | Zn  |
|----------------------------------|------|-----|------|------|------|-----|-----|-----|-----|-----|
| <b>Density/g cm<sup>-3</sup></b> | 3.43 | 4.1 | 6.07 | 7.19 | 7.21 | 7.8 | 8.7 | 8.9 | 8.9 | 7.1 |

(e) In 3d series highest density – Cu    lowest density – Sc

(f) Some important orders of density



## Electronic configurations and some other properties of the first series of transition elements

| Element                                                                      | Sc         | Ti         | v          | Cr         | Mn         | Fe         | Co         | Ni            | Cu            | Zn            |
|------------------------------------------------------------------------------|------------|------------|------------|------------|------------|------------|------------|---------------|---------------|---------------|
| Atomic number                                                                | 21         | 22         | 23         | 24         | 25         | 26         | 27         | 28            | 29            | 30            |
| Electronic configuration                                                     |            |            |            |            |            |            |            |               |               |               |
| M                                                                            | $3d^14s^2$ | $3d^24s^2$ | $3d^34s^2$ | $3d^54s^2$ | $3d^54s^2$ | $3d^64s^2$ | $3d^74s^2$ | $3d^{10}4s^2$ | $3d^{10}4s^1$ | $3d^{10}4s^2$ |
| M <sup>+</sup>                                                               | $3d^14s^1$ | $3d^24s^1$ | $3d^34s^1$ | $3d^5$     | $3d^54s^1$ | $3d^64s^1$ | $3d^74s^1$ | $3d^84s^1$    | $3d^{10}$     | $3d^{10}4s^1$ |
| M <sup>2+</sup>                                                              | $3d^1$     | $3d^2$     | $3d^3$     | $3d^4$     | $3d^5$     | $3d^6$     | $3d^7$     | $3d^8$        | $3d^9$        | $3d^{10}$     |
| M <sup>3+</sup>                                                              | [Ar]       | $3d^1$     | $3d^2$     | $3d^3$     | $3d^4$     | $3d^5$     | $3d^6$     | $3d^7$        | —             | —             |
| Enthalpy of atomisation, Δ <sub>a</sub> H <sup>Θ</sup> /kJ mol <sup>-1</sup> | 326        | 473        | 515        | 397        | 281        | 416        | 425        | 430           | 339           | 126           |
| Ionisation Enthalpy, Δ <sub>i</sub> H <sup>Θ</sup> /kJ mol <sup>-1</sup>     |            |            |            |            |            |            |            |               |               |               |
| Δ <sub>i</sub> H <sup>Θ</sup>                                                |            |            |            |            |            |            |            |               |               |               |
| I                                                                            | 631        | 656        | 650        | 653        | 717        | 762        | 758        | 736           | 745           | 906           |
| II                                                                           | 1235       | 1309       | 1414       | 1592       | 1509       | 1561       | 1644       | 1752          | 1958          | 1734          |
| III                                                                          | 2393       | 2657       | 2833       | 2990       | 3260       | 2962       | 3243       | 3402          | 3556          | 3829          |
| Metallic/Ionic radii/pm                                                      |            |            |            |            |            |            |            |               |               |               |
| M                                                                            | 164        | 147        | 135        | 129        | 137        | 126        | 125        | 125           | 128           | 137           |
| M <sup>2+</sup>                                                              | —          | —          | 79         | 82         | 82         | 77         | 74         | 70            | 73            | 75            |
| M <sup>3+</sup>                                                              | 73         | 67         | 64         | 62         | 65         | 65         | 61         | 60            | —             | —             |
| Standard electrode potential E <sup>Θ</sup> /V                               |            |            |            |            |            |            |            |               |               |               |
| M <sup>2+</sup> /M                                                           | —          | -1.63      | -1.18      | -0.90      | -1.18      | -0.44      | -0.28      | -0.25         | +0.34         | -0.76         |
| M <sup>3+</sup> /M <sup>2+</sup>                                             | —          | -0.37      | -0.26      | -0.41      | +1.57      | +0.77      | +1.97      | —             | —             | —             |
| Density/g cm <sup>-3</sup>                                                   | 3.43       | 4.1        | 6.07       | 7.19       | 7.21       | 7.8        | 8.7        | 8.9           | 8.9           | 7.1           |

### VARIABLE OXIDATION STATES POSSIBLE :

- (1) The elements which give the greatest number of oxidation states occur in or near the middle of the series. Manganese, for example, exhibits all the oxidation states from +2 to +7.
- (2) The lesser number of oxidation states at the extreme ends stems from either too few electrons to lose or share (Sc, Ti) or too many d electrons (hence fewer orbitals available in which to share electrons with others) for higher valence (Cu, Zn).
- (3) Thus, early in the series scandium(II) is virtually unknown and titanium(IV) is more stable than Ti(III) or Ti(II).
- (4) At the other end, the only oxidation state of zinc is +2 (no d electrons are involved).
- (5) The maximum oxidation states of reasonable stability correspond in value to the sum of the s and d electrons upto manganese ( $\text{Ti}^{\text{IV}}\text{O}_2$ ,  $\text{V}^{\text{V}}\text{O}_2^+$ ,  $\text{Cr}^{\text{VI}}\text{O}_4^{2-}$ ,  $\text{Mn}^{\text{VII}}\text{O}_4^-$ ) followed by a rather abrupt decrease in stability of higher oxidation states, so that the typical species to follow are  $\text{Fe}^{\text{II,III}}$ ,  $\text{Co}^{\text{II,III}}$ ,  $\text{Ni}^{\text{II}}$ ,  $\text{Cu}^{\text{I,II}}$ ,  $\text{Zn}^{\text{II}}$ .

- (6) The variability of oxidation states, a characteristic of transition elements, arises out of incomplete filling of d orbitals in such a way that their oxidation states differ from each other by unity, e.g.,  $V^{II}$ ,  $V^{III}$ ,  $V^{IV}$ ,  $V^V$ .
- (7) This is in contrast with the variability of oxidation states of non transition elements where oxidation states normally differ by a unit of two.
- (8) An interesting feature in the variability of oxidation states of the d-block elements is noticed among the groups (groups 4 through 10).
- (9) In group 6, Mo(VI) and W(VI) are found to be more stable than Cr(VI). Thus Cr(VI) in the form of dichromate in acidic medium is a strong oxidising agent, whereas  $MoO_3$  and  $WO_3$  are not.
- (10) Low oxidation states are found when a complex compound has ligands capable of  $\pi$ -acceptor character in addition to the  $\sigma$ -bonding. For example, in  $Ni(CO)_4$  and  $Fe(CO)_5$ , the oxidation state of nickel and iron is zero.
- (11) As the oxidation number of a metal increases, ionic character decreases. In the case of Mn,  $Mn_2O_7$  is a covalent green oil. Even  $CrO_3$  and  $V_2O_5$  have low melting points. In these higher oxides, the acidic character is predominant. Thus,  $Mn_2O_7$  gives  $HMnO_4$  and  $CrO_3$  gives  $H_2CrO_4$  and  $H_2Cr_2O_7$ .  $V_2O_5$  is, however, amphoteric though mainly acidic and it gives  $VO_4^{3-}$  as well as  $VO_2^+$  salts. In vanadium there is gradual change from the basic  $V_2O_3$  to less basic  $V_2O_4$  and to amphoteric  $V_2O_5$ .  $V_2O_4$  dissolves in acids to give  $VO^{2+}$  salts. Similarly,  $V_2O_5$  reacts with alkalis as well as acids to give  $VO_4^{3-}$  and  $VO_2^+$  respectively. The well characterised CrO is basic but  $Cr_2O_3$  is amphoteric.

### Oxidation states of the 1<sup>st</sup> transition series

most common ones are in bold types :

| Sc | Ti | V  | Cr | Mn | Fe | Co | Ni | Cu | Zn |
|----|----|----|----|----|----|----|----|----|----|
|    |    |    | +1 |    |    |    |    | +1 |    |
|    | +2 | +2 | +2 | +2 | +2 | +2 | +2 | +2 | +2 |
| +3 | +3 | +3 | +3 | +3 | +3 | +3 | +3 |    |    |
|    | +4 | +4 | +4 | +4 | +4 | +4 | +4 |    |    |
|    |    | +5 | +5 | +5 |    |    |    |    |    |
|    |    |    | +6 | +6 | +6 |    |    |    |    |
|    |    |    |    | +7 |    |    |    |    |    |

### Trends in stability of higher oxidation state :

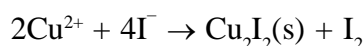
- (1) Table shows the stable halides of the 3d series of transition metals. The highest oxidation numbers are achieved in  $TiX_4$  (tetrahalides),  $VF_5$  and  $CrF_6$ . The +7 state for Mn is not represented in simple halides but  $MnO_3F$  is known, and beyond Mn no metal has a trihalide except  $FeX_3$  and  $CoF_3$ .
- (2) The ability of fluorine to stabilise the highest oxidation state is due to either higher lattice energy as in the case of  $CoF_3$ , or higher bond enthalpy terms for the higher covalent compounds, e.g.,  $VF_5$  and  $CrF_6$ .
- (3) Although  $V^V$  is represented only by  $VF_5$ , the other halides, however, undergo hydrolysis to give oxohalides,  $VOX_3$ .
- (4) Another feature of fluorides is their instability in the low oxidation states e.g.,  $VX_2$  ( $X = Cl, Br$  or  $I$ )

### Formulas of halides of 3d-metals

| Oxidation Number |                                 |                              |                  |                  |                               |                  |                  |                                |                  |
|------------------|---------------------------------|------------------------------|------------------|------------------|-------------------------------|------------------|------------------|--------------------------------|------------------|
| + 6              |                                 |                              | CrF <sub>6</sub> |                  |                               |                  |                  |                                |                  |
| + 5              |                                 | VF <sub>5</sub>              | CrF <sub>5</sub> |                  |                               |                  |                  |                                |                  |
| + 4              | TiX <sub>4</sub>                | VX <sub>4</sub> <sup>I</sup> | CrX <sub>4</sub> | MnF <sub>4</sub> |                               |                  |                  |                                |                  |
| + 3              | TiX <sub>3</sub>                | VX <sub>3</sub>              | CrX <sub>3</sub> | MnF <sub>3</sub> | FeX <sub>3</sub> <sup>I</sup> | CoF <sub>3</sub> |                  |                                |                  |
| + 2              | TiX <sub>2</sub> <sup>III</sup> | VX <sub>2</sub>              | CrX <sub>2</sub> | MnX <sub>2</sub> | FeX <sub>2</sub>              | CoX <sub>2</sub> | NiX <sub>2</sub> | CuX <sub>2</sub> <sup>II</sup> | ZnX <sub>2</sub> |
| + 1              |                                 |                              |                  |                  |                               |                  |                  | CuX <sup>III</sup>             |                  |

Key : X = F → I ; X<sup>I</sup> = F → Br ; X<sup>II</sup> = F → Cl ; X<sup>III</sup> = Cl → I

and the same applies to CuX. On the other hand, all Cu(II) halides are known except the iodide. In this case, Cu<sup>2+</sup> oxidises I<sup>-</sup> to I<sub>2</sub>:



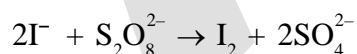
- (5) However, many copper (I) compounds are unstable in aqueous solution and undergo disproportionation.



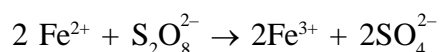
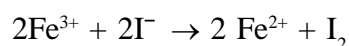
- (6) The stability of Cu<sup>2+</sup>(aq) rather than Cu<sup>+</sup>(aq) is due to the much more negative  $\Delta_{\text{Hyd}}H^{\ominus}$  of Cu<sup>2+</sup>(aq) than Cu<sup>+</sup>, which more than compensates for the second ionisation enthalpy of Cu.
- (7) The ability of oxygen to stabilise the highest oxidation state is demonstrated in the oxides.
- (8) The highest oxidation number in the oxides coincides with the group number and is attained in Sc<sub>2</sub>O<sub>3</sub> to Mn<sub>2</sub>O<sub>7</sub>.
- (9) Beyond Group 7, no higher oxides of Fe above Fe<sub>2</sub>O<sub>3</sub>, are known, although ferrates (VI)(FeO<sub>4</sub>)<sup>2-</sup>, are formed in alkaline media but they readily decompose to Fe<sub>2</sub>O<sub>3</sub> and O<sub>2</sub>.
- (10) Besides the oxides, oxocations stabilise V<sup>v</sup> as VO<sub>2</sub><sup>+</sup>, V<sup>IV</sup> as VO<sup>2+</sup> and Ti<sup>IV</sup> as TiO<sup>2+</sup>.
- (11) The ability of oxygen to stabilise these high oxidation states exceeds that of fluorine. Thus the highest Mn fluoride is MnF<sub>4</sub> whereas the highest oxide is Mn<sub>2</sub>O<sub>7</sub>. The ability of oxygen to form multiple bonds to metals explains its superiority.
- (12) In the covalent oxide Mn<sub>2</sub>O<sub>7</sub>, each Mn is tetrahedrally surrounded by O's including a Mn–O–Mn bridge.
- (13) The tetrahedral [MO<sub>4</sub>]<sup>n</sup> ions are known for V<sup>V</sup>, Cr<sup>VI</sup>, Mn<sup>V</sup>, Mn<sup>VI</sup> and Mn<sup>VII</sup>.

**FORMATION OF COLOURED ION :****Colour : (aquated)** $\text{Ti}^{4+} \longrightarrow \text{colourless}$  $\text{V}^{4+} \longrightarrow \text{blue}$  $\text{V}^{2+} \longrightarrow \text{violet}$  $\text{Cr}^{3+} \longrightarrow \text{violet}$  $\text{Mn}^{2+} \longrightarrow \text{light pink}$  $\text{Fe}^{3+} \longrightarrow \text{yellow}$  $\text{Ni}^{2+} \longrightarrow \text{green}$  $\text{Zn}^{2+} \longrightarrow \text{colourless}$  $\text{Sc}^{3+} \longrightarrow \text{colourless}$  $\text{Ti}^{3+} \longrightarrow \text{purple}$  $\text{V}^{3+} \longrightarrow \text{green}$  $\text{Cr}^{2+} \longrightarrow \text{blue}$  $\text{Mn}^{3+} \longrightarrow \text{violet}$  $\text{Fe}^{2+} \longrightarrow \text{light green}$  $\text{Co}^{2+} \longrightarrow \text{pink}$  $\text{Cu}^{2+} \longrightarrow \text{blue}$ **CATALYTIC PROPERTIES**

- (1) The transition metals and their compounds are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states and to form complexes. Vanadium(V) oxide (in Contact Process), finely divided iron (in Haber's Process), and nickel (in Catalytic Hydrogenation) are some of the examples.
- (2) Catalysts at a solid surface involve the formation of bonds between reactant molecules and atoms of the surface of the catalyst (first row transition metals utilise 3d and 4s electrons for bonding).
- (3) This has the effect of increasing the concentration of the reactants at the catalyst surface and also weakening of the bonds in the reacting molecules (the activation energy is lowering).
- (4) Also because the transition metal ions can change their oxidation states, they become more effective as catalysts. For example, iron(III) catalyses the reaction between iodide and persulphate ions.



An explanation of this catalytic action can be given as:



| Catalyst                                               | Used                                                                                                                                                                                                                       |
|--------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| $\text{TiCl}_3 \longrightarrow$                        | Used as the Ziegler-Natta catalyst in the production of polythene.                                                                                                                                                         |
| $\text{V}_2\text{O}_5 \longrightarrow$                 | Convert $\text{SO}_2$ to $\text{SO}_3$ in the contact process for making $\text{H}_2\text{SO}_4$                                                                                                                           |
| $\text{MnO}_2 \longrightarrow$                         | Used as a catalyst to decompose $\text{KClO}_3$ to give $\text{O}_2$                                                                                                                                                       |
| $\text{Fe} \longrightarrow$                            | Promoted iron is used in the Haber-Bosch process for making $\text{NH}_3$                                                                                                                                                  |
| $\text{FeCl}_3 \longrightarrow$                        | Used in the production of $\text{CCl}_4$ from $\text{CS}_2$ and $\text{Cl}_2$                                                                                                                                              |
| $\text{PdCl}_2 \longrightarrow$                        | Wacker process for converting $\text{C}_2\text{H}_4 + \text{H}_2\text{O} + \text{PdCl}_2$ to $\text{CH}_3\text{CHO} + 2\text{HCl} + \text{Pd}$ .                                                                           |
| $\text{Pd} \longrightarrow$                            | Used for hydrogenation (e.g. phenol to cyclohexanone).                                                                                                                                                                     |
| $\text{Pt/PtO} \longrightarrow$                        | Adams catalyst, used for reductions.                                                                                                                                                                                       |
| $\text{Pt} \longrightarrow$                            | Formerly used for $\text{SO}_2 \longrightarrow \text{SO}_3$ in the contact process for making $\text{H}_2\text{SO}_4$                                                                                                      |
| $\text{Pt/Rh} \longrightarrow$                         | Formerly used in the Ostwald process for making $\text{HNO}_3$ to oxidize $\text{NH}_3$ to $\text{NO}$                                                                                                                     |
| $\text{Cu} \longrightarrow$                            | Is used in the direct process for manufacture of $(\text{CH}_3)_2\text{SiCl}_2$ used to make silicones.                                                                                                                    |
| $\text{Cu/V} \longrightarrow$                          | Oxidation of cyclohexanol/cyclohexanone mixture to adipic acid which is used to make nylon-66                                                                                                                              |
| $\text{CuCl}_2 \longrightarrow$                        | Deacon process of making $\text{Cl}_2$ from $\text{HCl}$                                                                                                                                                                   |
| $\text{Ni} \longrightarrow$                            | Raney nickel, numerous reduction processes (e.g. manufacture of hexamethylenediamine, production of $\text{H}_2$ from $\text{NH}_3$ , reducing anthraquinone to anthraquinol in the production of $\text{H}_2\text{O}_2$ ) |
| $\text{FeSO}_4 + \text{H}_2\text{O}_2 \longrightarrow$ | Used as Fenton's reagent for oxidizing alcohols to aldehydes.                                                                                                                                                              |

### Formation of Interstitial Compounds

Interstitial compounds are those which are formed when small atoms like H, C or N are trapped inside the crystal lattices of metals. The principal physical and chemical characteristics of these compounds are as follows:

- They have high melting points, higher than those of pure metals.
- They are very hard, some borides approach diamond in hardness.
- They retain metallic conductivity.
- They are chemically inert.

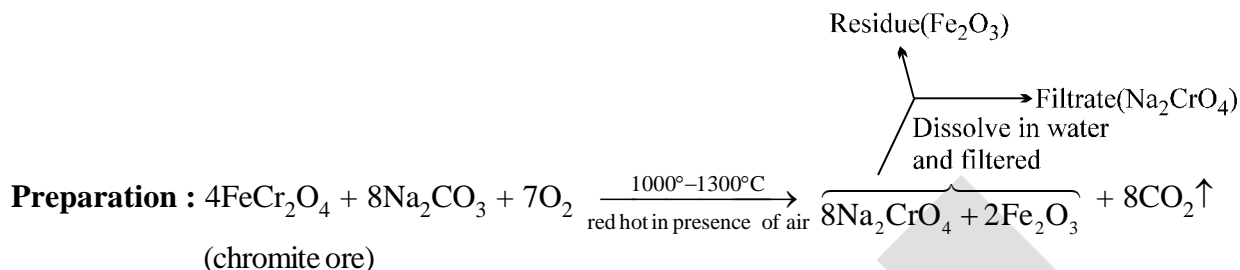
### Alloy Formation

An alloy is a blend of metals prepared by mixing the components. Alloys may be homogeneous solid solutions in which the atoms of one metal are distributed randomly among the atoms of the other. Such alloys are formed by atoms with metallic radii that are within about 15 percent of each other. Because of similar radii and other characteristics of transition metals, alloys are readily formed by these metals. The alloys so formed are hard and have often high melting points.

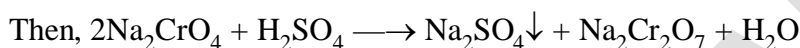


The best known are ferrous alloys: chromium, vanadium, tungsten, molybdenum and manganese are used for the production of a variety of steels and stainless steel. Alloys of transition metals with non transition metals such as brass (copper-zinc) and bronze (copper-tin), are also of considerable industrial importance.

### CHROMATE -DICHROMATE



[Lime ( $\text{CaO}$ ) added with  $\text{Na}_2\text{CO}_3$  which keeps the mass porous so that air has access to all parts and prevents fusion]



conc.

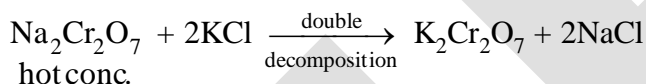
It's solubility  
 upto  $32^\circ\text{C}$  increases  
 and then decreases

Hence, suitable temp. is to be  
 employed to crystallise out  
 $\text{Na}_2\text{SO}_4$  first.

Then  $\text{Na}_2\text{Cr}_2\text{O}_7$  is crystallised out as  $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  on evaporation.

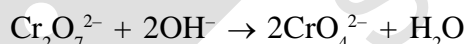
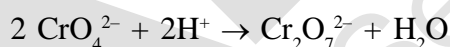
(red crystal)

#### How to get $\text{K}_2\text{Cr}_2\text{O}_7$ :



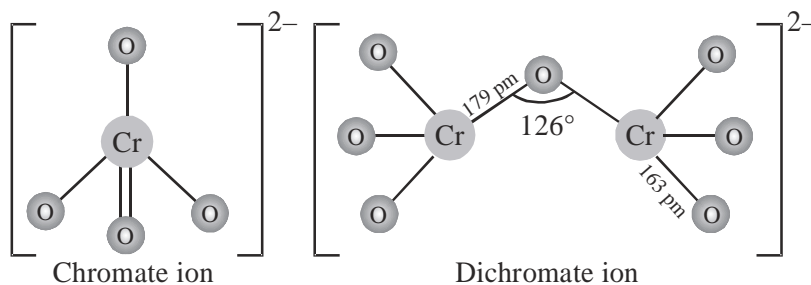
$\text{NaCl}$  crystallises out first and filtered off. Then  $\text{K}_2\text{Cr}_2\text{O}_7$  crystallised out on cooling

**The chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solution. The oxidation state of chromium in chromate and dichromate is the same.**

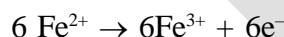
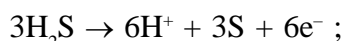
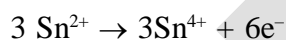
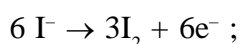


The structures of chromate ion,  $\text{CrO}_4^{2-}$  and the dichromate ion,  $\text{Cr}_2\text{O}_7^{2-}$  are shown below. The chromate ion is tetrahedral whereas the dichromate ion consists of two tetrahedra sharing one corner with  $\text{Cr}-\text{O}-\text{Cr}$  bond angle of  $126^\circ$ . Sodium and potassium dichromates are strong oxidising agents; the sodium salt has a greater solubility in water and is extensively used as an oxidising agent in organic chemistry. Potassium dichromate is used as a primary standard in volumetric analysis. In acidic solution, its oxidising action can be represented as follows:

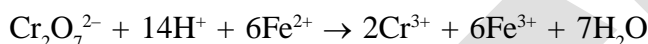




Thus, acidified potassium dichromate will oxidise iodides to iodine, sulphides to sulphur, tin(II) to tin(IV) and iron(II) salts to iron(III). The half-reactions are noted below:



The full ionic equation may be obtained by adding the half-reaction for potassium dichromate to the half-reaction for the reducing agent, for e.g.,



\* Similarities between hexavalent Cr & S-compounds :

- (i)  $\text{SO}_3$  &  $\text{CrO}_3 \longrightarrow$  both acidic.
- (ii)  $\text{S} \longrightarrow \text{SO}_4^{2-}$ ,  $\text{S}_2\text{O}_7^{2-}$ ,  $\text{Cr} \longrightarrow \text{CrO}_4^{2-}$ ,  $\text{Cr}_2\text{O}_7^{2-}$
- (iii)  $\text{CrO}_4^{2-}$  &  $\text{SO}_4^{2-}$  are isomorphous
- (iv)  $\text{SO}_2\text{Cl}_2$  &  $\text{CrO}_2\text{Cl}_2 \xrightarrow{\text{OH}^-} \text{SO}_4^{2-}$  &  $\text{CrO}_4^{2-}$  respectively.
- (v)  $\text{SO}_3\text{Cl}^-$  &  $\text{CrO}_3\text{Cl}^- \xrightarrow{\text{OH}^-} \text{SO}_4^{2-}$  &  $\text{CrO}_4^{2-}$
- (vi)  $\text{CrO}_3$  &  $\beta(\text{SO}_3)$  has same structure  $\begin{array}{ccccc} & \text{O} & & \text{O} & & \text{O} \\ & || & & || & & || \\ \text{---Cr} & \text{---O---} & \text{Cr---} & \text{O---} & \text{Cr---} \\ & || & & || & & || \\ & \text{O} & & \text{O} & & \text{O} \end{array}$

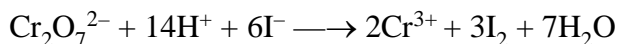
**Q. In laboratory  $\text{K}_2\text{Cr}_2\text{O}_7$  is used mainly not  $\text{Na}_2\text{Cr}_2\text{O}_7$ . Why?**

**Sol.**  $\text{Na}_2\text{Cr}_2\text{O}_7$  is deliquescent enough and changes its concentration and can not be taken as primary standard solution whereas  $\text{K}_2\text{Cr}_2\text{O}_7$  has no water of crystallisation and not deliquescent.

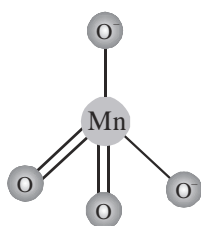
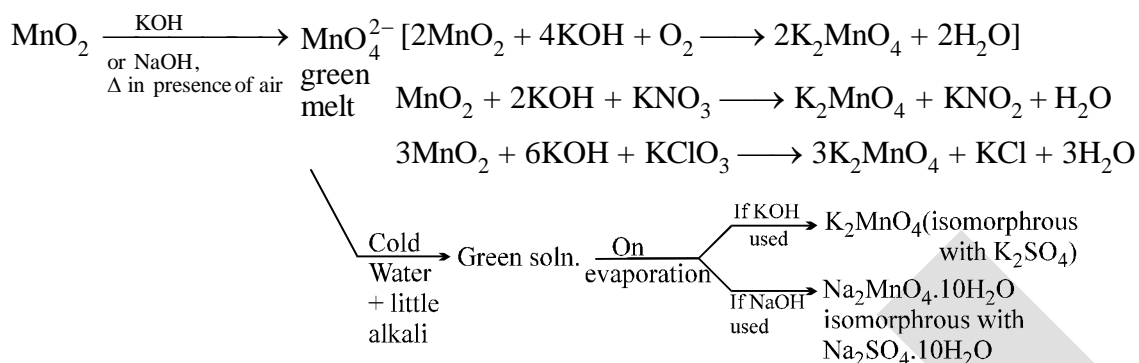
**Q. How to standardise  $\text{Na}_2\text{S}_2\text{O}_3$  solution in iodometry?**

**Sol.**  $\text{K}_2\text{Cr}_2\text{O}_7$  is primary standard  $\Rightarrow$  strength is known by weighing the salt in chemical balance and dissolving in measured amount of water.

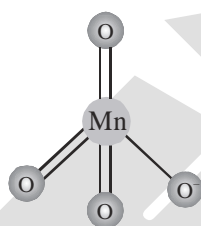
Then in acidic solution add. KI



This  $I_7$  is liberated can be estimated with  $S_7O_3^{2-}$ .

**MANGANATE & PERMANGANATE****PREPARATION OF MANGANATE ( $\text{MnO}_4^{2-}$ ) :-**

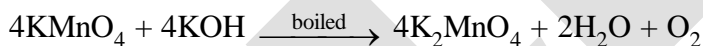
Tetrahedral manganate (green) ion



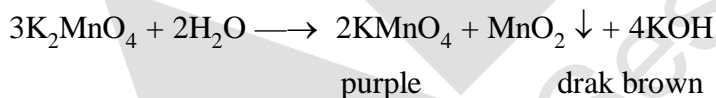
Tetrahedral permanganate (purple) ion

In presence of  $\text{KClO}_3$  &  $\text{KNO}_3$  the above reaction is more faster because these two on decomposition provides  $\text{O}_2$  easily.

Manganate is also obtained when  $\text{KMnO}_4$  is boiled with  $\text{KOH}$ .

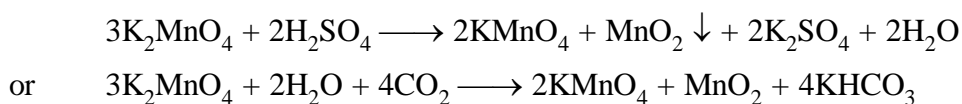


**Properties :** The above green solution is quite stable in alkali, but in pure water and in presence of acids, depositing  $\text{MnO}_2$  and giving a purple solution of permanganate.



**Prob. :**  $E^\circ_{\text{MnO}_4^{2-}/\text{MnO}_2} = 2.26 \text{ V}$  ;  $E^\circ_{\text{MnO}_4^{2-}/\text{MnO}_4^-} = -0.56 \text{ V}$

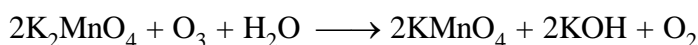
Prove that  $\text{MnO}_4^{2-}$  will disproportionate in acidic medium.

**Conversion of  $\text{MnO}_4^{2-}$  to  $\text{MnO}_4^-$** 

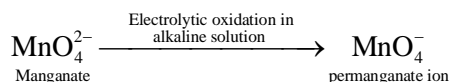
But in the above method  $\frac{1}{3}$  of Mn is lost as  $\text{MnO}_2$  but when oxidised either by  $\text{Cl}_2$  or by  $\text{O}_3$



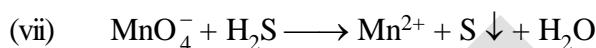
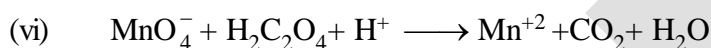
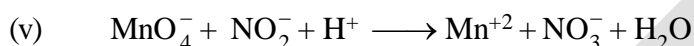
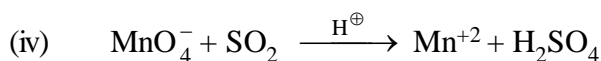
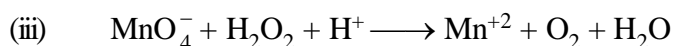
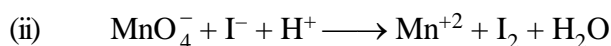
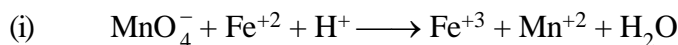
OR



OR



**Oxidising Prop. of  $\text{KMnO}_4$  : (in acidic medium)**

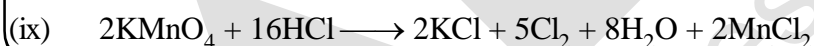


(1)\* It is not a primary standard since it is difficult to get it in a high degree of purity and free from traces of  $\text{MnO}_2$ .

(2)\* It is slowly reduced to  $\text{MnO}_2$  especially in presence of light or acid

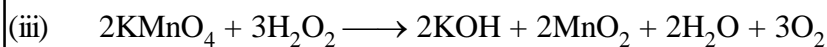
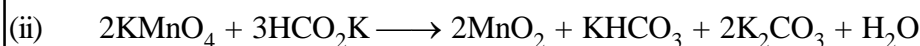
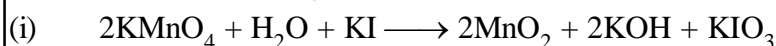


Hence it should be kept in dark bottles and standardise just before use.

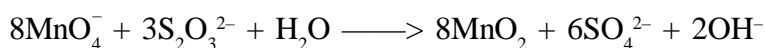


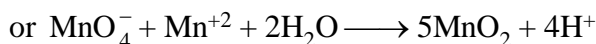
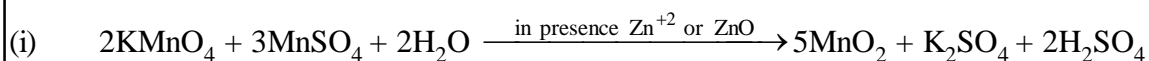
**Note:** Permanganate titrations in presence of hydrochloric acid are unsatisfactory since hydrochloric acid is oxidised to chlorine.

**Oxidising Prop. of  $\text{KMnO}_4$  in neutral or faintly alkaline solution.**



(iv) Thiosulphate is oxidised almost quantitatively to sulphate:



**Oxidising Prop. in neutral or weakly acidic solution:**

In absence of  $\text{Zn}^{+2}$  ions, some of the  $\text{Mn}^{+2}$  ion may escape, oxidation through the formation of insoluble  $\text{Mn}^{\text{II}}[\text{Mn}^{\text{IV}}\text{O}_3]$  manganous permanganite.

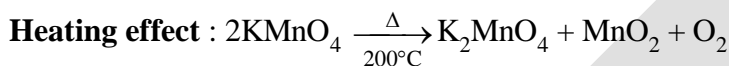
**Uses of  $\text{KMnO}_4$  :**

Besides its use in analytical chemistry, potassium permanganate is used as a favourite oxidant in preparative organic chemistry. Its uses for the bleaching of wool, cotton, silk and other textile fibres and for the decolourisation of oils are also dependent on its strong oxidising power.

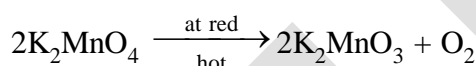
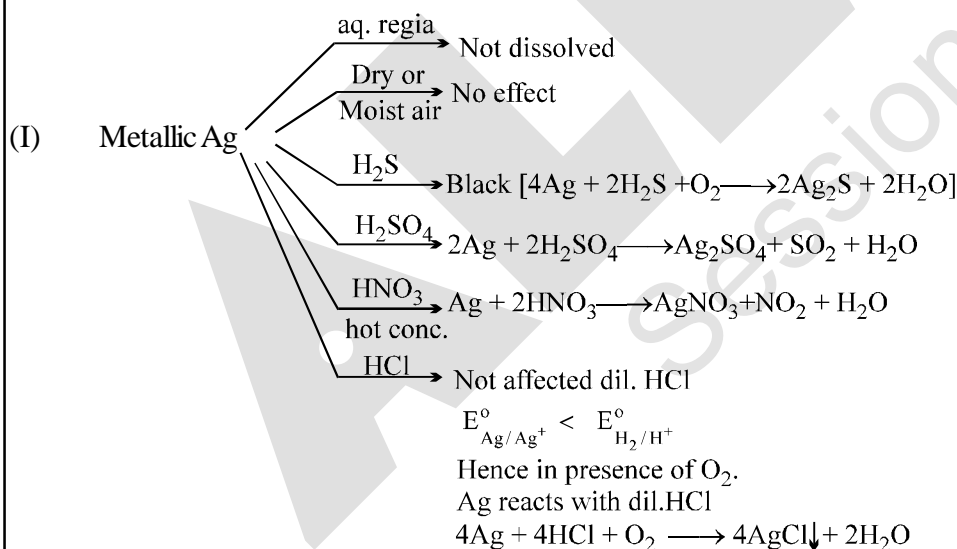
\*\*

In laboratory conversion of  $\text{Mn}^{+2}$  to  $\text{MnO}_4^-$  is done by :

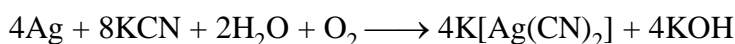
- (i)  $\text{PbO}_2$       (ii)  $\text{Pb}_3\text{O}_4 + \text{HNO}_3$       (iii)  $\text{Pb}_2\text{O}_3 + \text{HNO}_3$       (iv)  $\text{NaBiO}_3 / \text{H}^+$   
 (v)  $(\text{NH}_4)_2\text{S}_2\text{O}_8 / \text{H}^+$       (vi)  $\text{KIO}_4 / \text{H}^+$



green                  Black

**SILVER AND ITS COMPOUND**

In the same way in presence of  $\text{O}_2$ , Ag complexes with  $\text{NaCN} / \text{KCN}$ .

 **$\text{AgNO}_3$** 

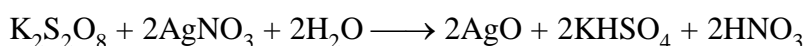
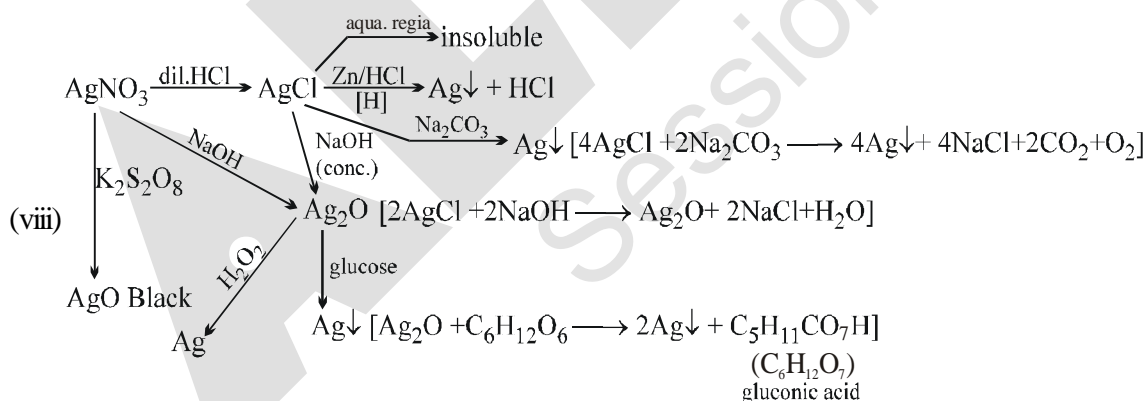
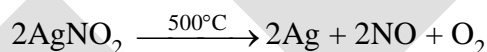
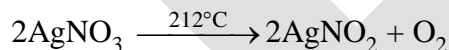
**Preparation :** Reaction of Ag with dilute  $\text{HNO}_3$  or conc.  $\text{HNO}_3$ .

**Properties :**

- (i) It is called as lunar caustic because in contact with skin it produces burning sensation like that of caustic soda with the formation of finely divided silver (black colour)
- (ii) Thermal decomposition :  $2\text{AgNO}_3(\text{s}) \rightarrow 2\text{Ag}(\text{s}) + \text{O}_2(\text{g}) + 2\text{NO}_2(\text{g})$
- (iii) Props. of  $\text{AgNO}_3$   
 $6\text{AgNO}_3 + 3\text{I}_2 + 3\text{H}_2\text{O} \longrightarrow 5\text{AgI} + \text{AgIO}_3 + 6\text{HNO}_3$   
 (excess)
- (iv)  $\text{Ag}_2\text{SO}_4 \xrightarrow{\Delta} 2\text{Ag} + \text{SO}_2 + \text{O}_2$
- (v)  $\text{A}(\text{AgNO}_3) \xrightarrow[\text{added}]{\text{B}}$  white ppt appears quickly  
 $\text{B}(\text{Na}_2\text{S}_2\text{O}_3) \xrightarrow[\text{added}]{\text{A}}$  It takes time to give white ppt. } Explain
- (vi)  $\text{Ag}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} \xrightarrow{\Delta} \text{Ag}_2\text{S} + \text{H}_2\text{SO}_4$   
 $\text{AgCl}, \text{AgBr}, \text{AgI}$  (but not  $\text{Ag}_2\text{S}$ ) are soluble in  $\text{Na}_2\text{S}_2\text{O}_3$  forming  $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{-3}$  complexes
- (vii)  $\text{AgBr} + \text{AgNO}_3 \xrightarrow{\text{KBr}} \text{AgBr} \downarrow + \text{KNO}_3$

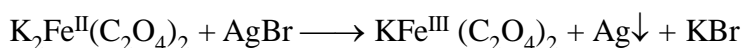
Pale yellow  
ppt.

**Heating effect :**

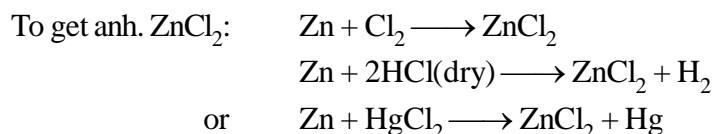
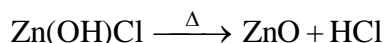


\*  $\text{AgO}$  supposed to be paramagnetic due to  $d^9$  configuration. But actually it is diamagnetic and exists as  $\text{Ag}^{\text{I}} [\text{Ag}^{\text{III}}\text{O}_2]$

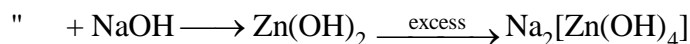
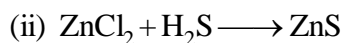
\* Reaction involved in developer :







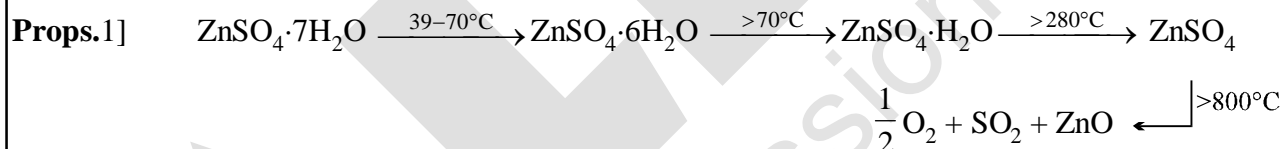
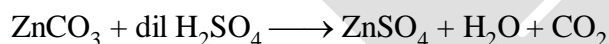
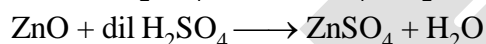
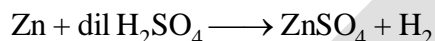
**Properties:** (i) It is deliquescent white solid (when anhydrous)



- Uses:** 1] Used for impregnating timber to prevent destruction by insects  
 2] As dehydrating agent when anhydrous  
 3]  $\text{ZnO} \cdot \text{ZnCl}_2$  used in dental filling

### **$\text{ZnSO}_4$**

Preparation:  $\rightarrow$

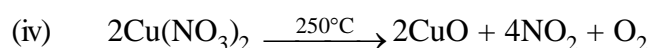
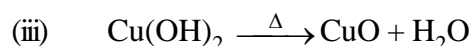


- Uses:** 1] in eye lotion  
 2] Lithophone ( $\text{ZnS} + \text{BaSO}_4$ ) is used as white pigment

### **COPPER COMPOUNDS**

#### **$\text{CuO}$**

**Preparation :** (i)  $\text{CuCO}_3 \cdot \text{Cu(OH)}_2 \xrightarrow{\Delta} 2\text{CuO} + \text{H}_2\text{O} + \text{CO}_2$  (Commercial process)  
 Malachite Green  
 (native Cu-carbonate)





- Properties :**
- (i) CuO is insoluble in water
  - (ii) Readily dissolves in dil. acids
 
$$\text{CuO} + \text{H}_2\text{SO}_4 \longrightarrow \text{CuSO}_4 + \text{H}_2\text{O}$$

$$\text{HCl} \longrightarrow \text{CuCl}_2$$

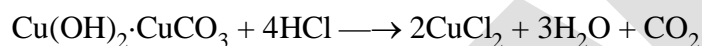
$$\text{HNO}_3 \longrightarrow \text{Cu}(\text{NO}_3)_2$$
  - (iii) It decomposes when, heated above  $1100^\circ\text{C}$ 

$$4\text{CuO} \longrightarrow 2\text{Cu}_2\text{O} + \text{O}_2$$
  - (iv) CuO is reduced to Cu by  $\text{H}_2$  or C under hot condition
 
$$\text{CuO} + \text{C} \longrightarrow \text{Cu} + \text{CO} \uparrow$$

$$\text{CuO} + \text{H}_2 \longrightarrow \text{Cu} + \text{H}_2\text{O} \uparrow$$

### CuCl<sub>2</sub>

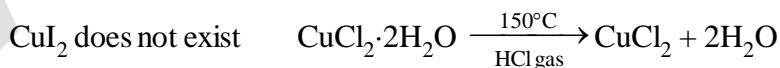
**Preparation:**  $\text{CuO} + 2\text{HCl}(\text{conc.}) \longrightarrow \text{CuCl}_2 + \text{H}_2\text{O}$



- Properties :**
- (i) It is crystallised as  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  of Emerald green colour
  - (ii) dil. solution in water is blue in colour due to formation of  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$  complex.
  - (iii) When conc. HCl or KCl added to dil. solution of  $\text{CuCl}_2$  the colour changes into yellow, owing to the formation of  $[\text{CuCl}_4]^{2-}$
  - (iv) The conc. aq. solution is green in colour having the two complex ions in equilibrium  $2[\text{Cu}(\text{H}_2\text{O})_4]\text{Cl}_2 \rightleftharpoons [\text{Cu}(\text{H}_2\text{O})_4]^{2+} + [\text{CuCl}_4]^{2-} + 4\text{H}_2\text{O}$
  - (v)  $\text{CuCl}_2 \longrightarrow \text{CuCl}$  by no. of reagents
    - (a)  $\text{CuCl}_2 + \text{Cu-turnings} \xrightarrow{\Delta} 2\text{CuCl}$
    - (b)  $2\text{CuCl}_2 + \text{H}_2\text{SO}_3 + \text{H}_2\text{O} \longrightarrow 2\text{CuCl} + 2\text{HCl} + 2\text{H}_2\text{SO}_4$
    - (c)  $2\text{CuCl}_2 + \text{Zn/HCl} \longrightarrow 2\text{CuCl} + \text{ZnCl}_2$
    - (d)  $\text{CuCl}_2 + \text{SnCl}_2 \longrightarrow \text{CuCl} + \text{SnCl}_4$

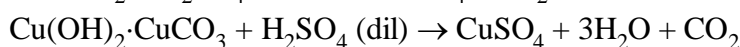
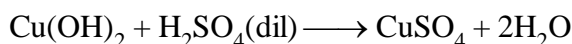
\*\*  $\text{CuF}_2 \cdot 2\text{H}_2\text{O} \longrightarrow$  light blue  
 $\text{CuCl}_2 \cdot 2\text{H}_2\text{O} \longrightarrow$  green  
 $\text{CuBr}_2 \longrightarrow$  almost black

$\left\{ \begin{array}{l} \text{Anh. CuCl}_2 \text{ is dark brown mass obtained} \\ \text{by heating } \text{CuCl}_2 \cdot 2\text{H}_2\text{O} \text{ at } 150^\circ\text{C} \text{ in presence} \\ \text{of HCl vap.} \end{array} \right.$



### CuSO<sub>4</sub>

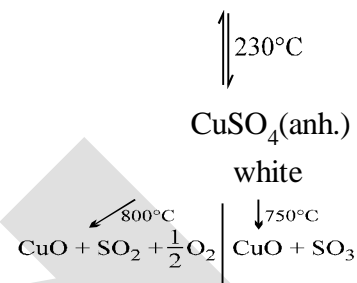
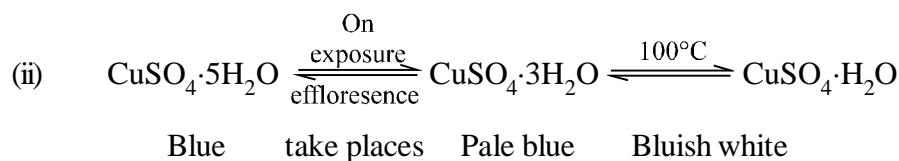
**Preparation :**  $\text{CuO} + \text{H}_2\text{SO}_4(\text{dil}) \longrightarrow \text{CuSO}_4 + \text{H}_2\text{O}$



(Scrap)

$\text{Cu} + \text{dil. H}_2\text{SO}_4 \longrightarrow$  no reaction { Cu is below H in electrochemical series }

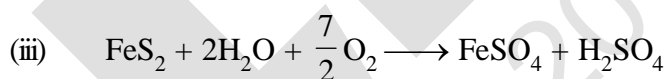
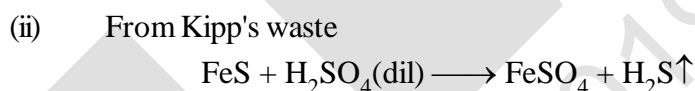
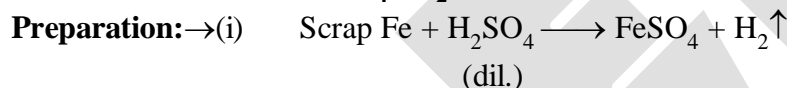
**Properties :** → (i) It is crystallised as  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$



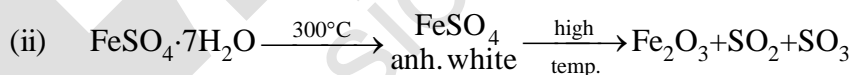
(iii) Revision with all others reagent

### IRON COMPOUNDS

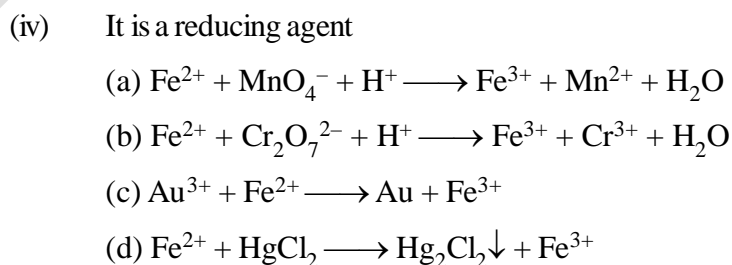
#### $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$



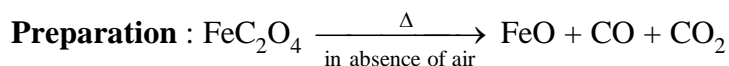
**Properties:** → (i) It undergoes aerial oxidation forming basic ferric sulphate  
 $4\text{FeSO}_4 + \text{H}_2\text{O} + \text{O}_2 \longrightarrow 4\text{Fe}(\text{OH})\text{SO}_4$



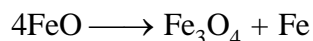
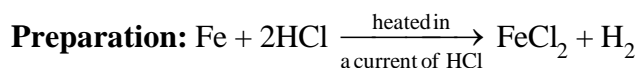
(iii) Aq. solution is acidic due to hydrolysis  
 $\text{FeSO}_4 + 2\text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_2 + \text{H}_2\text{SO}_4$   
 weak base



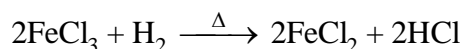
(v) It forms double salt. Example  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$

**FeO(Black)**

**Properties :** It is stable at high temperature and on cooling slowly disproportionates into  $\text{Fe}_3\text{O}_4$  and iron

**FeCl<sub>2</sub>**

OR



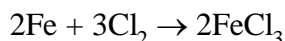
- Properties:** → (i) It is deliquescent in air like  $\text{FeCl}_3$
- (ii) It is soluble in water, alcohol and ether also because it is sufficiently covalent in nature
- (iii) It volatilises at about  $1000^\circ\text{C}$  and vapour density indicates the presence of  $\text{Fe}_2\text{Cl}_4$ . Above  $1300^\circ\text{C}$  density becomes normal
- (iv) It oxidises on heating in air
- $$12\text{FeCl}_2 + 3\text{O}_2 \longrightarrow 2\text{Fe}_2\text{O}_3 + 8\text{FeCl}_3$$
- (v)  $\text{H}_2$  evolves on heating in steam
- $$3\text{FeCl}_2 + 4\text{H}_2\text{O} \longrightarrow \text{Fe}_3\text{O}_4 + 6\text{HCl} + \text{H}_2$$
- (vi) It can exist as different hydrated form
- $$\text{FeCl}_2 \cdot 2\text{H}_2\text{O} \longrightarrow \text{colourless}$$
- $$\text{FeCl}_2 \cdot 4\text{H}_2\text{O} \longrightarrow \text{pale green}$$
- $$\text{FeCl}_2 \cdot 6\text{H}_2\text{O} \longrightarrow \text{green}$$

**Ferric Chloride ( $\text{FeCl}_3$ )**

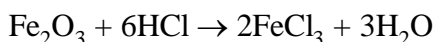
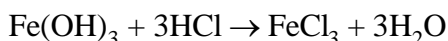
This is the most important ferric salt. It is known in anhydrous and hydrated forms. The hydrated form consists of six water molecules,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ .

**Preparation :**

- (i) Anhydrous ferric chloride is obtained by passing dry chlorine gas over heated iron fillings. The vapours are condensed in a bottle attached to the outlet of the tube.

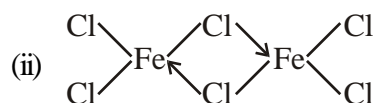
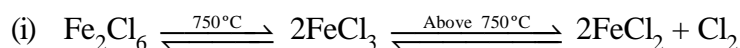


- (ii)  $\text{Fe}_2(\text{CO}_3)_3 + 6\text{HCl} \rightarrow 2\text{FeCl}_3 + 3\text{H}_2\text{O} + 3\text{CO}_2$

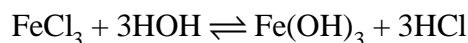


The solution on evaporation and cooling deposits yellow crystals of hydrated ferric chloride.  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$

**Properties**

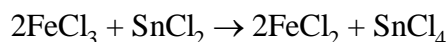


(iii) It dissolves in water. The solution is acidic in nature due to its hydrolysis as shown below :

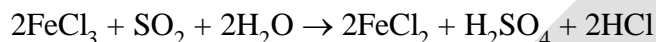


(v) Ferric chloride acts as an oxidising agent.

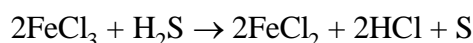
(a) It oxidises stannous chloride to stannic chloride.



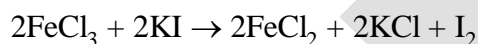
(b) It oxidises  $\text{SO}_2$  to  $\text{H}_2\text{SO}_4$



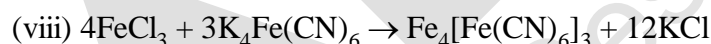
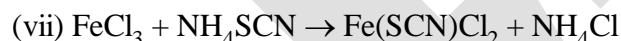
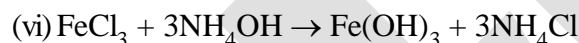
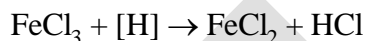
(c) It oxidises  $\text{H}_2\text{S}$  to S



(d) It liberates iodine from KI.



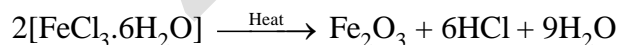
(e) Nascent hydrogen reduces  $\text{FeCl}_3$  into  $\text{FeCl}_2$



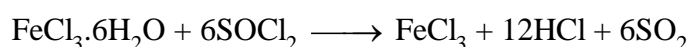
Prussian blue

(Ferri ferrocyanide)

(ix) On heating hydrated ferric chloride  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , anhydrous ferric chloride is not obtained. It is changed to  $\text{Fe}_2\text{O}_3$  with evolution of  $\text{H}_2\text{O}$  and  $\text{HCl}$ .



Hydrated ferric chloride may be dehydrated by heating with thionyl chloride.



## EXERCISE # O-1

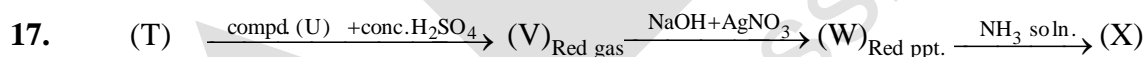
SELECT ONLY ONE IS CORRECT OPTIONS :

## General Properties of d-block

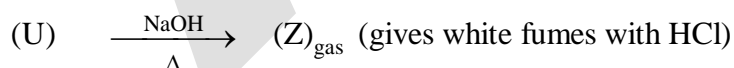
1.  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \xrightleftharpoons{\text{Fe} + \text{Mo}} 2\text{NH}_3(\text{g})$  ; Haber's process, Mo is used as  
(A) a catalyst (B) a catalytic promoter  
(C) an oxidising agent (D) as a catalytic poison
2. An ornamental of gold having 75% of gold, it is of ..... carat.  
(A) 18 (B) 16 (C) 24 (D) 20
3. Transition elements having more tendency to form complex than representative elements (s and p-block elements) due to -  
(A) availability of d-orbitals for bonding  
(B) variable oxidation states are not shown by transition elements  
(C) all electrons are paired in d-orbitals  
(D) f-orbitals are available for bonding
4. A compound of mercury used in cosmetics, in Ayurvedic and Yunani medicines and known as Vermilion is -  
(A)  $\text{HgCl}_2$  (B)  $\text{HgS}$  (C)  $\text{Hg}_2\text{Cl}_2$  (D)  $\text{HgI}$
5. Transition elements are usually characterised by variable oxidation states but Zn does not show this property because of  
(A) completion of np-orbitals (B) completion of (n-1)d orbitals  
(C) completion of ns-orbitals (D) inert pair effect
6. The d-block element which is a liquid at room temperature, having high specific heat, less reactivity than hydrogen and its chloride ( $\text{MX}_2$ ) is volatile on heating is  
(A) Cu (B) Hg (C) Ce (D) Pm
7. Coinage metals show the properties of  
(A) typical elements (B) normal elements  
(C) inner-transition elements (D) transition element
8. The transition metal used in X-rays tube is  
(A) Mo (B) Ta (C) Tc (D) Pm
9. The higher oxidation states of transition elements are found to be in the combination with A and B, which are  
(A) F, O (B) O, N (C) O, Cl (D) F, Cl
10. The metals present in insulin and haemoglobin are respectively  
(A) Zn, Hg (B) Zn, Fe (C) Co, Fe (D) Mg, Fe

11. A metal M which is not affected by strong acids like conc.  $\text{HNO}_3$ , conc.  $\text{H}_2\text{SO}_4$  and conc. solution of alkalis like NaOH, KOH forms  $\text{MCl}_3$  which finds use for toning in photography. The metal M is  
(A) Ag (B) Hg (C) Au (D) Cu
12. Manganese steel is used for making railway tracks because  
(A) it is hard with high percentage of Mn  
(B) it is soft with high percentage of Mn  
(C) it is hard with small concentration of manganese with impurities  
(D) it is soft with small concentration of manganese with impurities
13. Transition elements in lower oxidation states act as Lewis acid because  
(A) they form complexes (B) they are oxidising agents  
(C) they donate electrons (D) they do not show catalytic properties
14. The electrons which take part in order to exhibit variable oxidation states by transition metals are  
(A) ns only (B) (n-1)d only  
(C) ns and (n-1)d only but not np (D) (n-1)d and np only but not ns
15. Solution of  $\text{MnO}_4^-$  is purple-coloured due to  
(A) d-d-transition (B) charge transfer from O to Mn  
(C) due to both d-d-transition and charge transfer (D) none of these
16. An element of 3d-transition series shows two oxidation states x and y, differ by two units then  
(A) compounds in oxidation state x are ionic if  $x > y$   
(B) compounds in oxidation state x are ionic if  $x < y$   
(C) compounds in oxidation state y are covalent if  $x < y$   
(D) compounds in oxidation state y are covalent if  $y < x$

## Compounds of d-block



imparts violet  
colour in the  
flame test



sublimes on  
heating

**Identify (T) to (Z).**

- (A)  $T = \text{KMnO}_4$ ,  $U = \text{HCl}$ ,  $V = \text{Cl}_2$ ,  $W = \text{HgI}_2$ ,  $X = \text{Hg}(\text{NH}_2)\text{NO}_3$ ,  $Y = \text{Hg}_2\text{Cl}_2$ ,  $Z = \text{N}_2$   
 (B)  $T = \text{K}_2\text{Cr}_2\text{O}_7$ ,  $U = \text{NH}_4\text{Cl}$ ,  $V = \text{CrO}_2\text{Cl}_2$ ,  $W = \text{Ag}_2\text{CrO}_4$ ,  $X = [\text{Ag}(\text{NH}_3)_2]^+$ ,  $Y = \text{AgCl}$ ,  $Z = \text{NH}_3$   
 (C)  $T = \text{K}_2\text{CrO}_4$ ,  $U = \text{KCl}$ ,  $V = \text{CrO}_2\text{Cl}_2$ ,  $W = \text{HgI}_2$ ,  $X = \text{Na}_2\text{CrO}_4$ ,  $Y = \text{BaCO}_3$ ,  $Z = \text{NH}_4\text{Cl}$   
 (D)  $T = \text{KMnO}_4$ ,  $U = \text{NaCl}$ ,  $V = \text{CrO}_3$ ,  $W = \text{AgNO}_3$ ,  $X = (\text{NH}_4)_2\text{CrO}_4$ ,  $Y = \text{CaCO}_3$ ,  $Z = \text{SO}_2$

18. The number of moles of acidified  $\text{KMnO}_4$  required to convert one mole of sulphite ion into sulphate ion is  
 (A)  $2/5$  (B)  $3/5$  (C)  $4/5$  (D) 1
19.  $\text{Cr}_2\text{O}_7^{2-} \xrightleftharpoons[Y]{X} 2\text{CrO}_4^{2-}$ , X and Y are respectively  
 (A)  $\text{X} = \text{OH}^-$ ,  $\text{Y} = \text{H}^+$  (B)  $\text{X} = \text{H}^+$ ,  $\text{Y} = \text{OH}^-$   
 (C)  $\text{X} = \text{OH}^-$ ,  $\text{Y} = \text{H}_2\text{O}_2$  (D)  $\text{X} = \text{H}_2\text{O}_2$ ,  $\text{Y} = \text{OH}^-$
20.  $\text{CrO}_3$  dissolves in aqueous  $\text{NaOH}$  to give  
 (A)  $\text{Cr}_2\text{O}_7^{2-}$  (B)  $\text{CrO}_4^{2-}$  (C)  $\text{Cr}(\text{OH})_3$  (D)  $\text{Cr}(\text{OH})_2$
21. During estimation of oxalic acid Vs  $\text{KMnO}_4$ , self indicator is  
 (A)  $\text{KMnO}_4$  (B) oxalic acid (C)  $\text{K}_2\text{SO}_4$  (D)  $\text{MnSO}_4$
22. Acidified chromic acid +  $\text{H}_2\text{O}_2 \xrightarrow{\text{Org. solvent}} \text{X} + \text{Y}$ , X and Y are  
 (blue colour)  
 (A)  $\text{CrO}_5$  and  $\text{H}_2\text{O}$  (B)  $\text{Cr}_2\text{O}_3$  and  $\text{H}_2\text{O}$  (C)  $\text{CrO}_2$  and  $\text{H}_2\text{O}$  (D)  $\text{CrO}$  and  $\text{H}_2\text{O}$
23.  $\text{Y} \xleftarrow{\text{KI}} \text{CuSO}_4 \xrightarrow{\text{dil H}_2\text{SO}_4} \text{X}$  (Blue colour), X and Y are  
 (diatomic covalent molecule)  
 (A)  $\text{X} = \text{I}_2$ ,  $\text{Y} = [\text{Cu}(\text{H}_2\text{O})_4]^{2+}$  (B)  $\text{X} = [\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ ,  $\text{Y} = \text{I}_2$   
 (C)  $\text{X} = [\text{Cu}(\text{H}_2\text{O})_4]^+$ ,  $\text{Y} = \text{I}_2$  (D)  $\text{X} = [\text{Cu}(\text{H}_2\text{O})_5]^{2+}$ ,  $\text{Y} = \text{I}_2$
24.  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  (Ammonium dichromate) is used in fire works. The green coloured powder blown in air is  
 (A)  $\text{Cr}_2\text{O}_3$  (B)  $\text{CrO}_2$  (C)  $\text{Cr}_2\text{O}_4$  (D)  $\text{CrO}_3$
25. Iron becomes passive by ..... due to formation of .....  
 (A) dil.  $\text{HCl}$ ,  $\text{Fe}_2\text{O}_3$  (B) 80% conc.  $\text{HNO}_3$ ,  $\text{Fe}_3\text{O}_4$   
 (C) conc.  $\text{H}_2\text{SO}_4$ ,  $\text{Fe}_3\text{O}_4$  (D) conc.  $\text{HCl}$ ,  $\text{Fe}_3\text{O}_4$
26. Bayer's reagent used to detect olifinic double bond is  
 (A) acidified  $\text{KMnO}_4$  (B) aqueous  $\text{KMnO}_4$   
 (C) 1% alkaline  $\text{KMnO}_4$  solution (D)  $\text{KMnO}_4$  in benzene
27.  $\text{MnO}_4^- + xe^- \xrightarrow{\text{(Alkaline medium)}} \text{MnO}_4^{2-}$   
 $\quad \quad \quad + ye^- \xrightarrow{\text{(Acidic medium)}} \text{Mn}^{2+}$   
 $\quad \quad \quad + ze^- \xrightarrow{\text{(Neutral medium)}} \text{MnO}_2$   
 x, y and z are respectively  
 (A) 1, 2, 3 (B) 1, 5, 3 (C) 1, 3, 5 (D) 5, 3, 1
28.  $\text{Cu} + \text{conc. HNO}_3 \xrightarrow{\text{(hot)}} \text{Cu}(\text{NO}_3)_2 + \text{X}$  (oxide of nitrogen); then X is  
 (A)  $\text{N}_2\text{O}$  (B)  $\text{NO}_2$  (C)  $\text{NO}$  (D)  $\text{N}_2\text{O}_3$
29.  $\text{CuSO}_4$  solution reacts with excess  $\text{KCN}$  to give  
 (A)  $\text{Cu}(\text{CN})_2$  (B)  $\text{CuCN}$  (C)  $\text{K}_2[\text{Cu}(\text{CN})_2]$  (D)  $\text{K}_3[\text{Cu}(\text{CN})_4]$

30. Pick out the incorrect statement:
- (A)  $\text{MnO}_2$  dissolves in conc.  $\text{HCl}$ , but does not form  $\text{Mn}^{4+}$  ions  
 (B)  $\text{MnO}_2$  react with hot concentrated  $\text{H}_2\text{SO}_4$  liberating oxygen  
 (C)  $\text{K}_2\text{MnO}_4$  is formed when  $\text{MnO}_2$  in fused  $\text{KOH}$  is oxidised by air,  $\text{KNO}_3$ ,  $\text{PbO}_2$  or  $\text{NaBiO}_3$   
 (D) Decomposition of acidic  $\text{KMnO}_4$  is not catalysed by sunlight.
31. 1 mole of  $\text{Fe}^{2+}$  ions are oxidised to  $\text{Fe}^{3+}$  ions with the help of (in acidic medium)
- (A)  $1/5$  moles of  $\text{KMnO}_4$  (B)  $5/3$  moles of  $\text{KMnO}_4$   
 (C)  $2/5$  moles of  $\text{KMnO}_4$  (D)  $5/2$  moles of  $\text{KMnO}_4$
32. To an acidified dichromate solution, a pinch of  $\text{Na}_2\text{O}_2$  is added and shaken. What is observed:
- (A) blue colour (B) Orange colour changing to green  
 (C) Copious evolution of oxygen (D) Bluish - green precipitate
33. The rusting of iron is formulated as  $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$  which involves the formation of
- (A)  $\text{Fe}_2\text{O}_3$  (B)  $\text{Fe}(\text{OH})_3$  (C)  $\text{Fe}(\text{OH})_2$  (D)  $\text{Fe}_2\text{O}_3 + \text{Fe}(\text{OH})_3$
34. Solid  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  having covalent, ionic as well as co-ordinate bonds. Copper atom/ion forms ..... co-ordinate bonds with water.
- (A) 1 (B) 2 (C) 3 (D) 4
35.  $\text{KMnO}_4 + \text{HCl} \longrightarrow \text{H}_2\text{O} + \text{X}(\text{g})$ , X is a (acidified)
- (A) red liquid (B) violet gas  
 (C) greenish yellow gas (D) yellow-brown gas
36. Purple of cassius is:
- (A) Pure gold (B) Colloidal solution of gold  
 (C) Gold (I) hydroxide (D) Gold (III) chloride
37. Amongst the following species, maximum covalent character is exhibited by
- (A)  $\text{FeCl}_2$  (B)  $\text{ZnCl}_2$  (C)  $\text{HgCl}_2$  (D)  $\text{CdCl}_2$
38. Number of moles of  $\text{SnCl}_2$  required for the reduction of 1 mole of  $\text{K}_2\text{Cr}_2\text{O}_7$  into  $\text{Cr}_2\text{O}_3$  is (in acidic medium)
- (A) 3 (B) 2 (C) 1 (D)  $1/3$
39. Pick out the incorrect statement:
- (A)  $\text{MnO}_4^{2-}$  is quite strongly oxidizing and stable only in very strong alkalies. In dilute alkali, neutral solutions, it disproportionates.  
 (B) In acidic solutions,  $\text{MnO}_4^-$  is reduced to  $\text{Mn}^{2+}$  and thus,  $\text{KMnO}_4$  is widely used as oxidising agent  
 (C)  $\text{KMnO}_4$  does not acts as oxidising agent in alkaline medium  
 (D)  $\text{KMnO}_4$  is manufactured by the fusion of pyrolusite ore with  $\text{KOH}$  in presence of air or  $\text{KNO}_3$ , followed by electrolytic oxidation in strongly alkaline solution.
40. The aqueous solution of  $\text{CuCrO}_4$  is green because it contains
- (A) green  $\text{Cu}^{2+}$  ions (B) green  $\text{CrO}_4^{2-}$  ions



- (C) blue  $\text{Cu}^{2+}$  ions and green  $\text{CrO}_4^{2-}$  ions      (D) blue  $\text{Cu}^{2+}$  ions and yellow  $\text{CrO}_4^{2-}$  ions
41. In nitroprusside ion, the iron exists as  $\text{Fe}^{2+}$  and NO as  $\text{NO}^+$  rather than  $\text{Fe}^{3+}$  and NO respectively. These forms of ions are established with the help of  
(A) magnetic moment in solid state      (B) thermal decomposition method  
(C) by reaction with KCN      (D) by action with  $\text{K}_2\text{SO}_4$
42. Which of the following reaction is possible at anode?  
(A)  $2\text{Cr}^{3+} + 7\text{H}_2\text{O} \longrightarrow \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+$       (B)  $\text{F}_2 \longrightarrow 2\text{F}^-$   
(C)  $\frac{1}{2}\text{O}_2 + 2\text{H}^+ \longrightarrow \text{H}_2\text{O}$       (D) None of these
43. Colourless solutions of the following four salts are placed separately in four different test tubes and a strip of copper is dipped in each one of these. Which solution will turn blue?  
(A)  $\text{KNO}_3$       (B)  $\text{AgNO}_3$       (C)  $\text{Zn}(\text{NO}_3)_2$       (D)  $\text{ZnSO}_4$
44. When acidified  $\text{KMnO}_4$  is added to hot oxalic acid solution, the decolourization is slow in the beginning, but becomes very rapid after some time. This is because:  
(A)  $\text{Mn}^{2+}$  acts as autocatalyst      (B)  $\text{CO}_2$  is formed as the product  
(C) Reaction is exothermic      (D)  $\text{MnO}_4^-$  catalyses the reaction
45. Metre scales are made-up of alloy  
(A) invar      (B) stainless steel      (C) elektron      (D) magnalium
46. The Ziegler-Natta catalyst used for polymerisation of ethene and styrene is  $\text{TiCl}_4 + (\text{C}_2\text{H}_5)_3\text{Al}$ , the catalysing species (active species) involved in the polymerisation is  
(A)  $\text{TiCl}_4$       (B)  $\text{TiCl}_3$       (C)  $\text{TiCl}_2$       (D)  $\text{TiCl}$
47. 'Bordeaux mixture' is used as a fungicide. It is a mixture of  
(A)  $\text{CaSO}_4 + \text{Cu}(\text{OH})_2$       (B)  $\text{CuSO}_4 + \text{Ca}(\text{OH})_2$   
(C)  $\text{CuSO}_4 + \text{CaO}$       (D)  $\text{CuO} + \text{CaO}$
48. Peacock ore is:  
(A)  $\text{FeS}_2$       (B)  $\text{CuFeS}_2$       (C)  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$       (D)  $\text{Cu}_5\text{FeS}_4$

## EXERCISE # O-2

## SELECT MORE THAN ONE IS CORRECT OPTIONS

## General Properties of d-block

- Potash alum is a double salt, its aqueous solution shows the characteristics of  
(A)  $\text{Al}^{3+}$  ions (B)  $\text{K}^+$  ions (C)  $\text{SO}_4^{2-}$  ions (D)  $\text{Al}^{3+}$  ions but not  $\text{K}^+$  ions
- Addition of non-metals like B and C to the interstitial sites of a transition metal results the metal  
(A) of more ductability (B) of less ductability  
(C) less malleable (D) of more hardness
- Mercury is a liquid at  $0^\circ\text{C}$  because of  
(A) very high ionisation energy (B) weak metallic bonds  
(C) high heat of hydration (D) high heat of sublimation
- The correct statement(s) about transition elements is/are  
(A) the most stable oxidation state is +3 and its stability decreases across the period  
(B) transition elements of 3d-series have almost same atomic sizes from Cr to Cu  
(C) the stability of +2 oxidation state increases across the period  
(D) some transition elements like Ni, Fe, Cr may show zero oxidation state in some of their compounds
- The ionisation energies of transition elements are  
(A) less than p-block elements (B) more than s-block elements  
(C) less than s-block elements (D) more than p-block elements
- The metal(s) which does/do not form amalgam is/are  
(A) Fe (B) Pt (C) Zn (D) Ag
- Which of the following statements concern with d-block metals?  
(A) compounds containing ions of transition elements are usually coloured  
(B) Zinc has lowest melting point among 3d-series elements  
(C) they show variable oxidation states, which differ by two units only  
(D) they easily form complexes
- The highest oxidation state among transition elements is  
(A) + 7 by Mn (B) + 8 by Os (C) + 8 by Ru (D) + 7 by Fe
- Amphoteric oxide(s) is/are  
(A)  $\text{Al}_2\text{O}_3$  (B)  $\text{SnO}$  (C)  $\text{ZnO}$  (D)  $\text{Fe}_2\text{O}_3$
- The catalytic activity of transition elements is related to their  
(A) variable oxidation states (B) free surface valencies  
(C) complex formation ability (D) magnetic moment
- In the equation:  $\text{M} + 8\text{CN}^- + 2\text{H}_2\text{O} + \text{O}_2 \longrightarrow 4[\text{M}(\text{CN})_2]^- + 4\text{OH}^-$ , metal M is  
(A) Ag (B) Au (C) Cu (D) Hg
- $\text{CuSO}_4(\text{aq}) + 4\text{NH}_3 \longrightarrow \text{X}$ , then X is  
(A)  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  (B) paramagnetic  
(C) coloured (D) of a magnetic moment of 1.73 BM
- Amphoteric oxide(s) of Mn is/are  
(A)  $\text{MnO}_2$  (B)  $\text{Mn}_3\text{O}_4$  (C)  $\text{Mn}_2\text{O}_7$  (D)  $\text{MnO}$
- The lanthanide contraction is responsible for the fact that  
(A) Zr and Hf have same atomic sizes (B) Zr and Hf have same properties  
(C) Zr and Hf have different atomic sizes (D) Zr and Hf have different properties

15. Ion(s) having non zero magnetic moment (spin only) is/are  
(A)  $\text{Sc}^{3+}$  (B)  $\text{Ti}^{3+}$  (C)  $\text{Cu}^{2+}$  (D)  $\text{Zn}^{2+}$

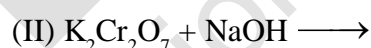
**Compounds of d-block**

16. Correct statement(s) is/are  
(A) an acidified solution of  $\text{K}_2\text{Cr}_2\text{O}_7$  liberates iodine from KI  
(B)  $\text{K}_2\text{Cr}_2\text{O}_7$  is used as a standard solution for estimation of  $\text{Fe}^{2+}$  ions  
(C) in acidic medium,  $M = N/6$  for  $\text{K}_2\text{Cr}_2\text{O}_7$   
(D)  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  on heating decomposes to yield  $\text{Cr}_2\text{O}_3$  through an endothermic reaction
17. Interstitial compounds are formed by  
(A) Co (B) Ni (C) Fe (D) Ca
18. Acidified  $\text{KMnO}_4$  can be decolourised by  
(A)  $\text{SO}_2$  (B)  $\text{H}_2\text{O}_2$  (C)  $\text{FeSO}_4$  (D)  $\text{Fe}_2(\text{SO}_4)_3$

EXERCISE # S-1

NUMERICAL GRID TYPE QUESTIONS :

- When mixture of NaCl and  $K_2Cr_2O_7$  is gently warmed with conc.  $H_2SO_4$  then compound X is formed. What is the oxidation state of central atom of X.
- Number of ions which gives blue colour in aqueous state :  
 $V^{+4}, Ni^{+2}, Ti^{+3}, Co^{+2}, Fe^{+3}, Cu^{+2}$
- Define the oxidation states of Mn in product of the given reaction  
 $3K_2MnO_4 + 2H_2O + 4CO_2 \rightarrow 2X + Y + 4KHCO_3$   
If the oxidation state of Mn in product X and Y are  $n_1$  and  $n_2$  respectively. Then find out the value of  $(n_1 + n_2)$  -
- Find number of metal ion which can produce high spin and low spin octahedral complex :  
 $Sc^{+3}, Ti^{+3}, V^{+3}, Cr^{+3}, Mn^{+3}, Fe^{+3}, Co^{+3}, Ni^{+2}$
- How many non-axial d-orbitals are involved in hybridisation of  $CrO_2Cl_2$ .
- Find the number of species from the following which has magnetic moment value of 1.73 B.M.  
 $Fe^{2+}, Cu^{2+}, Ni^{2+}, NO_2, NO_2^-, Ti^{3+}$
- Total no. of moles of Mohr's salt are required for per mole of dichromate ions during volumetric analysis.
- Find number of reaction(s) in which no redox change takes place -

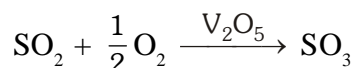


## EXERCISE # S-2

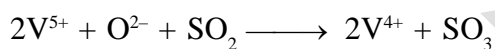
## COMPREHENSION TYPE QUESTIONS :

## Comprehension # 01 to 04

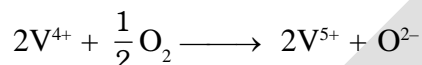
Transition metal and their compounds are used as catalysts in industry and in biological system. For example, in the Contact process, vanadium compounds in the +5 state ( $V_2O_5$  or  $VO_3^-$ ) are used to oxidise  $SO_2$  to  $SO_3$ :



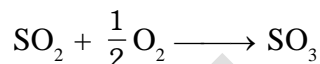
It is thought that the actual oxidation process takes place in two stages. In the first step,  $V^{5+}$  in the presence of oxide ions converts  $SO_2$  to  $SO_3$ . At the same time,  $V^{5+}$  is reduced to  $V^{4+}$ .



In the second step,  $V^{5+}$  is regenerated from  $V^{4+}$  by oxygen :



The overall process is, of course, the sum of these two steps:



- Transition metals and their compounds catalyse reactions because :
  - They have completely filled s-subshell
  - They have a comparable size due to poor shielding of d-subshell
  - They introduce an entirely new reaction mechanism with a lower activation energy
  - They have variable oxidation states differ by two units
- During the course of the reaction :
  - Catalyst undergoes changes in oxidation state
  - Catalyst increases the rate constant
  - Catalyst is regenerated in its original form when the reactants form the products
  - All are correct.
- Catalytic activity of transition metals depends on :
  - Their ability to exist in different oxidation states
  - The size of the metal atoms
  - The number of empty atomic orbitals available
  - None of these
- Which of the following ion involved in the above process will show paramagnetism?
 

|              |              |              |              |
|--------------|--------------|--------------|--------------|
| (A) $V^{5+}$ | (B) $V^{4+}$ | (C) $O^{2-}$ | (D) $VO_3^-$ |
|--------------|--------------|--------------|--------------|

**Comprehension # 05 & 06**

(X) is very important laboratory reagent which is prepared by its naturally occurring ore which is called pyrolusite. Pyrolusite when fused with alkali in the presence of  $O_2$ , green compound (Y) is produced. (Y) is converted into (X) by electrolysis or by using ozone.

5. On small scale (X) is prepared by disproportion of (Y) in acidic solution. Which of the following is produced by disproportion of (Y) in slight alkaline solution.
 

|                          |                            |
|--------------------------|----------------------------|
| (A) $KMnO_4$ , $Mn^{+2}$ | (B) $KMnO_4$ , $MnO_2$     |
| (C) $MnO_2$ , $Mn^{+2}$  | (D) $K_2MnO_4$ , $Mn^{+2}$ |
6. Select the correct statements :
  - (A) (X) is tetrahedral & diamagnetic
  - (B) (Y) is tetrahedral & paramagnetic
  - (C) (X) produce dimanganese hepta oxide (oily liquid) with conc.  $H_2SO_4$
  - (D) All are correct

**Comprehension # 07 to 09**

Due to availability of vacant orbitals of sufficiently low energy, d-block elements form complexes, d-block elements have different properties such as- catalytic, magnetic, alloy formation, interstitial compounds formation. Interstitial compounds are those compounds in which small atoms like carbon and boron fits into interstices of d-block elements crystal. In interstitial compounds, there is no chemical bond formation takes place so , chemical properties remain almost same but physical properties may change.

7. Which of the property of interstitial compounds has the same behaviour as that of the element -
 

|                            |               |
|----------------------------|---------------|
| (A) Malleability           | (B) Ductility |
| (C) Electrical conductance | (D) Hardness  |
8. Which of the following property gets decreased in interstitial compounds compared to that of the element -
 

|                  |                     |
|------------------|---------------------|
| (A) Malleability | (B) Metallic lustre |
| (C) Hardness     | (D) Density         |
9. Select correct statement -
  - (A) Highest oxidation state of 3d-series is +8.
  - (B) Ni, Cu and Zn are not transition element.
  - (C) Ziegler natta catalyst contain vanadium.
  - (D) Aq. solution of  $Cu^{2+}$ ,  $Fe^{+3}$  and  $Cr^{3+}$  are blue, yellow and green respectively.

**MATCH THE COLUMN : (Matrix Match)****10. Column-I (Metals)**

- (A) Zn  
(B) Cu  
(C) Ag  
(D) Au

**Column-II**

- (P) Cyanide process involve in the comerial extration  
(Q) Extracted by hydrometallurgical process  
(R) Roasting involve in the comerial extration  
(S) Present in Brass

**11. Column-I (catalyst)**

- (A)  $\text{TiCl}_4$   
(B)  $\text{PdCl}_2$   
(C)  $\text{Pt/PtO}$   
(D) Cu

**Column-II (Used)**

- (P) Adams catalyst in reduction  
(Q) In preparation of  $(\text{CH}_3)_2\text{SiCl}_2$   
(R) Used as the ziegler-natta catalyst in polythene production  
(S) Wacker process for converting  $\text{C}_2\text{H}_4$  to  $\text{CH}_3\text{CHO}$

**SELECT CORRECT CODE :****12. Column-I**

- (P)  $\text{Cr}_2\text{O}_3$   
(Q)  $\text{CrO}_3$   
(R)  $\text{Fe}_3\text{O}_4$   
(S)  $\text{N}_2\text{O}$

**Column-II**

- (1) Neutral oxide  
(2) Amphoteric oxide  
(3) Mix oxide  
(4) Acidic oxide

Select correct code for matching -

**Code :**

|     | P | Q | R | S |
|-----|---|---|---|---|
| (A) | 2 | 4 | 3 | 1 |
| (B) | 2 | 3 | 4 | 1 |
| (C) | 4 | 2 | 3 | 1 |
| (D) | 4 | 3 | 1 | 2 |

**13. Column-I**

**(Metal ion of 3d-series)**

- (P)  $\text{Ni}^{2+}$   
(Q)  $\text{Cr}^{2+}$   
(R)  $\text{V}^{2+}$   
(S)  $\text{Ti}^{4+}$

**Column-II**

**(Characterstic)**

- (1) produce blue aq. solution  
(2) half filled  $t_{2g}$  orbitals in octahedral complex  
(3) diamagnetic ion  
(4) calculated  $\mu = 2.84$  B.M. (spin only)

Select correct code for matching -

**Code :**

|     | P | Q | R | S |
|-----|---|---|---|---|
| (A) | 4 | 2 | 1 | 3 |
| (B) | 3 | 1 | 2 | 4 |
| (C) | 4 | 1 | 2 | 3 |
| (D) | 1 | 2 | 4 | 3 |

**ASSERTION & REASONING :**

Questions given below consist of two statements each printed as Assertion (A) and Reason (R); while answering these questions you are required to choose any one of the following four responses:

(A) if both (A) and (R) are true and (R) is the correct explanation of (A)

(B) if both (A) and (R) are true but (R) is not correct explanation of (A)

(C) if (A) is true but (R) is false

(D) if (A) is false and (R) is true

14. **Assertion** :  $\text{KMnO}_4$  is purple in colour due to charge transfer.

**Reason** : In  $\text{MnO}_4^-$ , there is no electron present in d-orbitals of manganese.

15. **Assertion** :  $\text{K}_2\text{CrO}_4$  has yellow colour due to charge transfer.

**Reason** :  $\text{CrO}_4^{2-}$  ion is tetrahedral in shape.

16. **Assertion** : The highest oxidation state of chromium in its compounds is +6.

**Reason** : Chromium atom has only six electrons in ns and (n-1) d orbitals.

17. **Assertion** :  $\text{CrO}_3$  reacts with HCl to form chromyl chloride gas.

**Reason** : Chromyl chloride ( $\text{CrO}_2\text{Cl}_2$ ) has tetrahedral shape.

18. **Assertion** : Zinc does not show characteristic properties of transition metals.

**Reason** : In zinc outermost shell is completely filled.

19. **Assertion** : Tungsten has a very high melting point.

**Reason** : Tungsten is a covalent compound.

20. **Assertion** : Equivalent mass of  $\text{KMnO}_4$  is equal to one-third of its molecular mass when it acts as an oxidising agent in an alkaline medium.

**Reason** : Oxidation number of Mn is +7 in  $\text{KMnO}_4$ .

21. **Assertion** :  $\text{Cu}^+$  ion is colourless.

**Reason** : Four water molecules are coordinated to  $\text{Cu}^+$  ion in water.



**MATCHING LIST TYPE 1 × 3 Q. (THREE LIST TYPE Q.)**

The following column 1, 2, 3 represent the different metals of 3d series and their properties

Answer the questions that follow

**Column-1 - Hexa aqua complex of dipositive ion of given metal**

**Column-2 - Magnetic moment (spin only)**

**Column-3 - Colour**

| Column - 1<br>Hexa aqua complex of dipositive<br>ion of given metal | Column - 2<br>Magnetic moment<br>(spin only) | Column - 3<br>Colour |
|---------------------------------------------------------------------|----------------------------------------------|----------------------|
| (I) Co                                                              | (i) $\sqrt{8}$ B.M.                          | (P) Green            |
| (II) Ni                                                             | (ii) $\sqrt{3}$ B.M.                         | (Q) Pink             |
| (III) V                                                             | (iii) $\sqrt{15}$ B.M.                       | (R) Colourless       |
| (IV) Zn                                                             | (iv) Zero                                    | (S) Violet           |
|                                                                     |                                              | (T) Blue             |

22. Select **CORRECT** combination for metal which have same magnetism as in  $[\text{Ti}(\text{H}_2\text{O})_6]^{4+}$   
 (A) (II), (iv), (R) (B) (I), (iv), (R) (C) (IV), (iv), (R) (D) (IV), (iv), (T)
23. Which is **CORRECT** magnetic moment and colour combination of the product when  $[\text{Co}(\text{H}_2\text{O})_6]^{+2}$  is react with conc. HCl solution  
 (A) (ii), (Q) (B) (ii), (T) (C) (iii), (Q) (D) (iii), (T)
24. Select **CORRECT** combination for hexaaqua complex of metal ion  $\text{M}^{+2}$  which have half filled  $t_{2g}$  configuration (i.e.  $t_{2g}^3$ )  
 (A) (III), (iii), (S) (B) (III), (iii), (P) (C) (III), (ii), (S) (D) (III), (iv), (P)
25.  $[\text{M}(\text{H}_2\text{O})_6]^{+2}$  of a metal in **column-1** have combination (i), (P) in **column-2, 3**. Select **CORRECT** combination for hexaammine complex of same metal ion.  
 (A) (i), (T) (B) (i), (S) (C) (iv), (R) (D) (iv) (T)

## EXERCISE # JEE-MAIN

- What would happen when a solution of potassium chromate is treated with an excess of dilute nitric acid  
- [AIEEE-2003]  
 (1)  $\text{Cr}^{3+}$  and  $\text{Cr}_2\text{O}_7^{2-}$  are formed (2)  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{H}_2\text{O}$  are formed  
 (3)  $\text{Cr}_2\text{O}_7^{2-}$  is reduced to +3 state of Cr (4)  $\text{Cr}_2\text{O}_7^{2-}$  is oxidised to +7 state of Cr
- Excess of KI reacts with  $\text{CuSO}_4$  solution and then  $\text{Na}_2\text{S}_2\text{O}_3$  solution is added to it. Which of the statements is incorrect for this reaction : [AIEEE-2004]  
 (1) Evolved  $\text{I}_2$  is reduced (2)  $\text{CuI}_2$  is formed  
 (3)  $\text{Na}_2\text{S}_2\text{O}_3$  is oxidised (4)  $\text{Cu}_2\text{I}_2$  is formed
- Calomel on reaction with  $\text{NH}_4\text{OH}$  gives [AIEEE-2004]  
 (1)  $\text{HgNH}_2\text{Cl}$  (2)  $\text{NH}_2\text{-Hg-Hg-Cl}$  (3)  $\text{Hg}_2\text{O}$  (4)  $\text{HgO}$
- In context with the transition elements, which of the following statements is incorrect? [AIEEE-2009]  
 (1) In the highest oxidation states of the first five transition elements (Sc to Mn), all the 4s and 3d electrons are used for bonding.  
 (2) Once the  $d^5$  configuration is exceeded, the tendency to involve all the 3d electrons in bonding decreases.  
 (3) In addition to the normal oxidation states, the zero oxidation state is also shown by these elements in complexes.  
 (4) In the highest oxidation states, the transition metal show basic character and form cationic complexes.
- Iron exhibits +2 and +3 oxidation states. Which of the following statements about iron is incorrect ? [AIEEE-2012]  
 (1) Ferrous compounds are more easily hydrolysed than the corresponding ferric compounds.  
 (2) Ferrous oxide is more basic in nature than the ferric oxide.  
 (3) Ferrous compounds are relatively more ionic than the corresponding ferric compounds.  
 (4) Ferrous compounds are less volatile than the corresponding ferric compounds.
- Consider the following reaction : [JEE MAIN-2013]  

$$x\text{MnO}_4^- + y\text{C}_2\text{O}_4^{2-} + z\text{H}^+ \rightarrow x\text{Mn}^{2+} + 2y\text{CO}_2 + \frac{z}{2} \text{H}_2\text{O}$$
 The values of x, y and z in the reaction are respectively :-  
 (1) 5, 2 and 16 (2) 2, 5 and 8 (3) 2, 5 and 16 (4) 5, 2 and 8
- Which of the following arrangements does not represent the correct order of the property stated against it ? [JEE MAIN-2013]  
 (1)  $\text{V}^{2+} < \text{Cr}^{2+} < \text{Mn}^{2+} < \text{Fe}^{2+}$  : paramagnetic behaviour  
 (2)  $\text{Ni}^{2+} < \text{Co}^{2+} < \text{Fe}^{2+} < \text{Mn}^{2+}$  : ionic size  
 (3)  $\text{Co}^{3+} < \text{Fe}^{3+} < \text{Cr}^{3+} < \text{Sc}^{3+}$  : stability in aqueous solution  
 (4)  $\text{Sc} < \text{Ti} < \text{Cr} < \text{Mn}$  : number of oxidation states
- Potassium dichromate when heated with concentrated sulphuric acid and a soluble chloride, gives brown - red vapours of: [JEE MAIN-2013, Online]  
 (1)  $\text{CrO}_3$  (2)  $\text{Cr}_2\text{O}_3$  (3)  $\text{CrCl}_3$  (4)  $\text{CrO}_2\text{Cl}_2$

9. The element with which of the following outer electron configuration may exhibit the largest number of oxidation states in its compounds : **[JEE MAIN-2013, Online]**  
 (1)  $3d^7 4s^2$  (2)  $3d^8 4s^2$  (3)  $3d^5 4s^2$  (4)  $3d^6 4s^2$
10. When a small amount of  $\text{KMnO}_4$  is added to concentrated  $\text{H}_2\text{SO}_4$ , a green oily compound is obtained which is highly explosive in nature. Compound may be : **[JEE MAIN-2013, Online]**  
 (1)  $\text{Mn}_2\text{O}_3$  (2)  $\text{MnSO}_4$  (3)  $\text{Mn}_2\text{O}_7$  (4)  $\text{MnO}_2$
11. Which series of reactions correctly represents chemical relations related to iron and its compound?  
 (1)  $\text{Fe} \xrightarrow{\text{Cl}_2, \text{heat}} \text{FeCl}_3 \xrightarrow{\text{heat, air}} \text{FeCl}_2 \xrightarrow{\text{Zn}} \text{Fe}$   
 (2)  $\text{Fe} \xrightarrow{\text{O}_2, \text{heat}} \text{Fe}_3\text{O}_4 \xrightarrow{\text{CO}, 600^\circ\text{C}} \text{FeO} \xrightarrow{\text{CO}, 700^\circ\text{C}} \text{Fe}$   
 (3)  $\text{Fe} \xrightarrow{\text{dil H}_2\text{SO}_4} \text{FeSO}_4 \xrightarrow{\text{H}_2\text{SO}_4, \text{O}_2} \text{Fe}_2(\text{SO}_4)_3 \xrightarrow{\text{Heat}} \text{Fe}$   
 (4)  $\text{Fe} \xrightarrow{\text{O}_2, \text{heat}} \text{FeO} \xrightarrow{\text{dil H}_2\text{SO}_4} \text{FeSO}_4 \xrightarrow{\text{Heat}} \text{Fe}$  **[JEE MAIN-2014]**
12. The equation which is balanced and represents the correct product (s) is : **[JEE MAIN-2014]**  
 (1)  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+} + (\text{EDTA})^{4-} \xrightarrow{\text{excess NaOH}} [\text{Mg}(\text{EDTA})]^{2-} + 6\text{H}_2\text{O}$   
 (2)  $\text{CuSO}_4 + 4\text{KCN} \rightarrow \text{K}_2[\text{Cu}(\text{CN})_4] + \text{K}_2\text{SO}_4$   
 (3)  $\text{Li}_2\text{O} + 2\text{KCl} \rightarrow 2\text{LiCl} + \text{K}_2\text{O}$   
 (4)  $[\text{CoCl}(\text{NH}_3)_5]^+ + 5\text{H}^+ \rightarrow \text{Co}^{2+} + 5\text{NH}_4^+ + \text{Cl}^-$
13. Which of the following is **not** formed when  $\text{H}_2\text{S}$  reacts with acidic  $\text{K}_2\text{Cr}_2\text{O}_7$  solution ?  
 (1)  $\text{K}_2\text{SO}_4$  (2)  $\text{Cr}_2(\text{SO}_4)_3$   
 (3) S (4)  $\text{CrSO}_4$  **[JEE MAIN-2014, Online]**
14. Copper becomes green when exposed to moist air for a long period. This is due to :- **[JEE MAIN-2014, Online]**  
 (1) the formation of a layer of cupric oxide on the surface of copper.  
 (2) the formation of basic copper sulphate layer on the surface of the metal  
 (3) the formation of a layer of cupric hydroxide on the surface of copper.  
 (4) the formation of a layer of basic carbonate of copper on the surface of copper.
15. Which one of the following exhibits the largest number of oxidation states ? **[JEE MAIN-2014, Online]**  
 (1) Mn(25) (2) V(23) (3) Cr (24) (4) Ti (22)
16. How many electrons are involved in the following redox reaction ? **[JEE MAINS-2014, Online]**  
 $\text{Cr}_2\text{O}_7^{2-} + \text{Fe}^{2+} + \text{C}_2\text{O}_4^{2-} \rightarrow \text{Cr}^{3+} + \text{Fe}^{3+} + \text{CO}_2$  (Unbalanced)  
 (1) 3 (2) 4 (3) 5 (4) 6
17. Amongst the following, identify the species with an atom in +6 oxidation state: **[JEE MAIN-2014, Online]**  
 (1)  $[\text{MnO}_4]^-$  (2)  $[\text{Cr}(\text{CN})_6]^{3-}$  (3)  $\text{Cr}_2\text{O}_3$  (4)  $\text{CrO}_2\text{Cl}_2$

18. Match the catalysts to the correct processes :-

[JEE MAIN-2015]

|     | Catalyst               |       | Process                      |
|-----|------------------------|-------|------------------------------|
| (A) | $\text{TiCl}_3$        | (i)   | Wacker process               |
| (B) | $\text{PdCl}_2$        | (ii)  | Ziegler-Natta polymerization |
| (C) | $\text{CuCl}_2$        | (iii) | Contact process              |
| (D) | $\text{V}_2\text{O}_5$ | (iv)  | Deacon's process             |

- (1) A-ii, B-iii, C-iv, D-i  
 (2) A-iii, B-i, C-ii, D-iv  
 (3) A-iii, B-ii, C-iv, D-i  
 (4) A-ii, B-i, C-iv, D-iii

19. Which of the following statements is false :-

[JEE MAIN-2015, Online]

- (1)  $\text{Cr}_2\text{O}_7^{2-}$  has a Cr – O – Cr bond  
 (2)  $\text{CrO}_4^{2-}$  is tetrahedral in shape  
 (3)  $\text{Na}_2\text{Cr}_2\text{O}_7$  is a primary standard in volumetry  
 (4)  $\text{K}_2\text{Cr}_2\text{O}_7$  is less soluble than  $\text{Na}_2\text{Cr}_2\text{O}_7$

20. The transition metal ions responsible for colour in ruby and emerald are, respectively :

[Jee Main 2016]

- (1)  $\text{Cr}^{3+}$  and  $\text{Cr}^{3+}$  (2)  $\text{Cr}^{3+}$  and  $\text{Co}^{3+}$  (3)  $\text{Co}^{3+}$  and  $\text{Cr}^{3+}$  (4)  $\text{Co}^{3+}$  and  $\text{Co}^{3+}$

21. Galvanization is applying a coating of :-

[Jee Main 2016]

- (1) Zn (2) Pb (3) Cr (4) Cu

22. Which of the following compounds is metallic and ferromagnetic ?

[Jee Main 2016]

- (1)  $\text{MnO}_2$  (2)  $\text{TiO}_2$  (3)  $\text{CrO}_2$  (4)  $\text{VO}_2$

23. Which one of the following species is stable in aqueous solution?

[Jee Main 2016]

- (1)  $\text{MnO}_4^{3-}$  (2)  $\text{MnO}_4^{2-}$  (3)  $\text{Cu}^+$  (4)  $\text{Cr}^{2+}$

24. What will occur if a block of copper metal is dropped into a beaker containing a solution of 1M  $\text{ZnSO}_4$  ?

- (1) The copper metal will dissolve and zinc metal will be deposited

[Jee Main 2016]

- (2) No reaction will occur  
 (3) The copper metal will dissolve with evolution of oxygen gas  
 (4) The copper metal will dissolve with evolution of hydrogen gas

25. Which of the following ions does **not** liberate hydrogen gas on reaction with dilute acids?

[JEE MAIN-2017, Online]

- (1)  $\text{Ti}^{2+}$  (2)  $\text{Cr}^{2+}$  (3)  $\text{Mn}^{2+}$  (4)  $\text{V}^{2+}$

26. In the following reactions, ZnO is respectively acting as a/an : [JEE MAIN-2017]



- (1) base and acid (2) base and base  
 (3) acid and acid (4) acid and base

## EXERCISE # JEE-ADVANCED

## TRUE/FALSE :

1.  $\text{Cu}^+$  disproportionates to  $\text{Cu}^{2+}$  and elemental copper in solution. [JEE 1991]

## FILL IN THE BLANKS :

2. When  $\text{Fe(s)}$  is dissolved in aqueous hydrochloric acid in a closed vessel, the work done is ..... [JEE 1997]  
 3. Silver jewellery items tarnish slowly in the air due to their reaction with ..... [JEE 1997]

## MULTIPLE CHOICE QUESTIONS WITH ONE CORRECT ANSWER :

4. Which one is solder ? [JEE 1995]  
 (A) Cu and Pb (B) Zn and Cu (C) Pb and Sn (D) Fe and Zn  
 5. Which compound does not dissolve in hot, dilute  $\text{HNO}_3$ ? [JEE 1996]  
 (A)  $\text{HgS}$  (B)  $\text{PbS}$  (C)  $\text{CuS}$  (D)  $\text{CdS}$   
 6. Ammonium dichromate is used in some fireworks. The green coloured powder blown in the air is - [JEE 1997]  
 (A)  $\text{CrO}_3$  (B)  $\text{Cr}_2\text{O}_3$  (C)  $\text{Cr}$  (D)  $\text{CrO}(\text{O}_2)$   
 7. The number of moles of  $\text{KMnO}_4$  that will be needed to react with one mole of sulphite ion in acidic solution is - [JEE 1997]  
 (A)  $2/5$  (B)  $3/5$  (C)  $4/5$  (D) 1  
 8. Read the following statement and explanation and answer as per the options given below : [JEE 1998]

**Assertion :**  $\text{Zn}^{2+}$  is diamagnetic.

**Reason :** Two electrons are lost from 4s orbital to form  $\text{Zn}^{2+}$ .

- (A) If both assertion and reason are correct, and reason is the correct explanation of the assertion.  
 (B) If both assertion and reason are correct, but reason is not the correct explanation of the assertion.  
 (C) If assertion is correct but reason is incorrect.  
 (D) If assertion is incorrect but reason is correct.
9. In the dichromate anion, [JEE 1999]  
 (A) 4 Cr – O bonds are equivalent (B) 6 Cr – O bonds are equivalent  
 (C) all Cr – O bonds are equivalent (D) all Cr – O bonds are non-equivalent
10. Anhydrous ferric chloride is prepared by: [JEE 2002]  
 (A) heating hydrated ferric chloride at a high temperature in a stream of air  
 (B) heating metallic iron in a stream of dry chlorine gas  
 (C) reaction of ferric oxide with  $\text{HCl}$   
 (D) reaction of metallic iron with  $\text{HCl}$
11. When  $\text{MnO}_2$  is fused with  $\text{KOH}$ , a coloured compound is formed, the product and its colour is: [JEE 2003]  
 (A)  $\text{K}_2\text{MnO}_4$ , green (B)  $\text{KMnO}_4$ , purple  
 (C)  $\text{Mn}_2\text{O}_3$ , brown (D)  $\text{Mn}_3\text{O}_4$ , black
12. The product of oxidation of  $\text{I}^-$  with  $\text{MnO}_4^-$  in alkaline medium is - [JEE 2004]  
 (A)  $\text{IO}_3^-$  (B)  $\text{I}_2$  (C)  $\text{IO}^-$  (D)  $\text{IO}_4^-$

13.  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  on heating liberates a gas. The same gas will be obtained by - [JEE 2004]  
 (A) heating  $\text{NH}_4\text{NO}_2$  (B) heating  $\text{NH}_4\text{NO}_3$   
 (C) treating  $\text{H}_2\text{O}_2$  with  $\text{NaNO}_2$  (D) treating  $\text{Mg}_3\text{N}_2$  with  $\text{H}_2\text{O}$
14. Which of the following combination will produce  $\text{H}_2$  gas ? [JEE Advance 2017]  
 (A) Zn metal and  $\text{NaOH(aq)}$  (B) Au metal and  $\text{NaCN(aq)}$  in the presence of air  
 (C) Cu metal and conc.  $\text{HNO}_3$  (D) Fe metal and conc.  $\text{HNO}_3$

**MULTIPLE CHOICE QUESTIONS WITH ONE OR MORE THAN ONE CORRECT ANSWER :**

15. Which of the following alloys contains (s) Cu and Zn ? [JEE 1993]  
 (A) Bronze (B) Brass (C) Gun metal (D) Type metal
16. Addition of high proportions of manganese makes steel useful in making rails of railroads, because manganese. [JEE 1998]  
 (A) gives hardness to steel  
 (B) helps the formation of oxides of iron  
 (C) can remove oxygen and sulphur  
 (D) can show highest oxidation state of +7.
17. The correct statement(s) about  $\text{Cr}^{2+}$  and  $\text{Mn}^{3+}$  is (are) [JEE Advance 2015]  
 [Atomic numbers of Cr = 24 and Mn = 25]  
 (A)  $\text{Cr}^{2+}$  is a reducing agent  
 (B)  $\text{Mn}^{3+}$  is an oxidizing agent  
 (C) Both  $\text{Cr}^{2+}$  and  $\text{Mn}^{3+}$  exhibit  $d^4$  electronic configuration  
 (D) When  $\text{Cr}^{2+}$  is used as a reducing agent, the chromium ion attains  $d^5$  electronic configuration
18. Fusion of  $\text{MnO}_2$  with  $\text{KOH}$  in presence of  $\text{O}_2$  produces a salt **W**. Alkaline solution of **W** upon electrolytic oxidation yields another salt **X**. The manganese containing ions present in **W** and **X**, respectively, are **Y** and **Z**. Correct statement(s) is (are) [JEE Advance 2019]  
 (A) **Y** is diamagnetic in nature while **Z** is paramagnetic  
 (B) Both **Y** and **Z** are coloured and have tetrahedral shape  
 (C) In both **Y** and **Z**,  $\pi$ -bonding occurs between p-orbitals of oxygen and d-orbitals of manganese.  
 (D) In aqueous acidic solution, **Y** undergoes disproportionation reaction to give **Z** and  $\text{MnO}_2$ .
19. Consider the following reactions (unbalanced) [JEE Advance 2019]  
 $\text{Zn} + \text{hot conc. H}_2\text{SO}_4 \rightarrow \text{G} + \text{R} + \text{X}$   
 $\text{Zn} + \text{conc. NaOH} \rightarrow \text{T} + \text{Q}$   
 $\text{G} + \text{H}_2\text{S} + \text{NH}_4\text{OH} \rightarrow \text{Z (a precipitate)} + \text{X} + \text{Y}$   
 Choose the correct option(s).  
 (A) The oxidation state of Zn in T is +1  
 (B) Bond order of Q is 1 in its ground state  
 (C) Z is dirty white in colour  
 (D) R is a V-shaped molecule

## ANSWER KEY

## EXERCISE # O-1

- |         |         |         |           |
|---------|---------|---------|-----------|
| 1. (B)  | 2. (A)  | 3. (A)  | 4. (B)    |
| 5. (B)  | 6. (B)  | 7. (D)  | 8. (A)    |
| 9. (A)  | 10. (B) | 11. (C) | 12. (A)   |
| 13. (A) | 14. (C) | 15. (B) | 16. (B,C) |
| 17. (B) | 18. (A) | 19. (A) | 20. (B)   |
| 21. (A) | 22. (A) | 23. (B) | 24. (A)   |
| 25. (B) | 26. (C) | 27. (B) | 28. (B)   |
| 29. (D) | 30. (D) | 31. (A) | 32. (A,C) |
| 33. (D) | 34. (D) | 35. (C) | 36. (B)   |
| 37. (C) | 38. (A) | 39. (C) | 40. (D)   |
| 41. (A) | 42. (A) | 43. (B) | 44. (A)   |
| 45. (A) | 46. (B) | 47. (B) | 48. (D)   |

## EXERCISE # O-2

- |               |               |              |                  |
|---------------|---------------|--------------|------------------|
| 1. (A, B, C)  | 2. (B, C, D)  | 3. (A, B)    | 4. (A, C, D)     |
| 5. (A, B)     | 6. (A, B)     | 7. (A, B, D) | 8. (B, C)        |
| 9. (A, B, C)  | 10. (A, B, C) | 11. (A, B)   | 12. (A, B, C, D) |
| 13. (A, B)    | 14. (A, B)    | 15. (B, C)   | 16. (A, B, C)    |
| 17. (A, B, C) | 18. (A, B, C) |              |                  |

## EXERCISE # S-1

- (6), In this reaction  $\text{CrO}_2\text{Cl}_2$  is formed in which Cr is +6.
  - (2),  $\text{V}^{+4}$ ,  $\text{Cu}^{+2}$
  - (11), +7, +4
  - (3),  $\text{Mn}^{+3}$ ,  $\text{Fe}^{+3}$ ,  $\text{Co}^{+3}$
  - $\text{CrO}_2\text{Cl}_2$  has  $d^3s$  hybridisation and all 3d-orbitals are non-axial which are  $d_{xy}$ ;  $d_{yz}$  and  $d_{xz}$ .
  - (003)
  - (6), Mohr's salt  

$$\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$$

$$6 \text{Fe}^{+2} + \text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+ \rightarrow 2\text{Cr}^{+3} + 7\text{H}_2\text{O} + 6\text{Fe}^{+3}$$
  - 3
- (I)  $\text{BaCl}_2 + \text{Na}_2\text{CrO}_4 \xrightarrow{\text{CH}_3\text{COOH}} \text{BaCrO}_4 \downarrow + 2\text{NaCl}$
- (II)  $\text{K}_2\text{Cr}_2\text{O}_7 + \text{NaOH} \longrightarrow \text{K}_2\text{CrO}_4$   

$$\text{CrO}_4^{2-} \xrightleftharpoons[\text{OH}^-]{\text{H}^+} \text{Cr}_2\text{O}_7^{2-}$$
- (III)  $\text{Cr}_2\text{O}_7^{2-} + \text{NO}_3^- \xrightarrow{\text{H}^+} \text{no reaction.}$
- (IV)  $\text{Cr}_2\text{O}_7^{2-} + \text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{H}^+} \text{CH}_3 - \text{COOH} + \text{Cr}^{+3}$

## EXERCISE # S-2

- |                                           |                                                   |         |         |
|-------------------------------------------|---------------------------------------------------|---------|---------|
| 1. (C)                                    | 2. (D)                                            | 3. (A)  | 4. (B)  |
| 5. (B)                                    | 6. (D)                                            | 7. (C)  | 8. (A)  |
| 9. (D)                                    | 10. (A)-(R,S) ; (B)-(R,S) ; (C)-(P,Q) ; (D)-(P,Q) |         |         |
| 11. (A)-(R) ; (B)-(S) ; (C)-(P) ; (D)-(Q) |                                                   | 12. (A) | 13. (C) |
| 14. (B)                                   | 15. (B)                                           | 16. (A) | 17.(B)  |
| 18. (C)                                   | 19. (C)                                           | 20. (B) | 21. (C) |
| 22. (C)                                   | 23. (D)                                           | 24. (A) | 25. (A) |

## EXERCISE # JEE-MAIN

- |         |         |         |                 |
|---------|---------|---------|-----------------|
| 1. (2)  | 2. (2)  | 3. (1)  | 4. (4)          |
| 5. (1)  | 6. (3)  | 7. (1)  | 8. (4)          |
| 9. (3)  | 10. (3) | 11. (2) | 12. (4)         |
| 13. (4) | 14. (4) | 15. (1) | 16. (4)         |
| 17. (4) | 18. (4) | 19. (3) | 20. (1)         |
| 21. (1) | 22. (3) | 23. (2) | 24. (2)         |
|         |         |         | 25. (3) 26. (4) |

## EXERCISE # JEE-ADVANCED

**TRUE/FALSE :**

- 1. True**

### FILL IN THE BLANKS:

- 2.** Zero

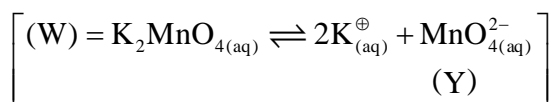
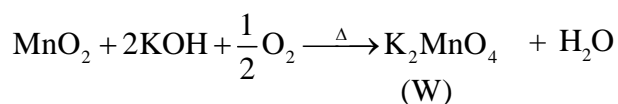
**3.** H<sub>2</sub>S

**MULTIPLE CHOICE QUESTIONS WITH ONE CORRECT ANSWER:**

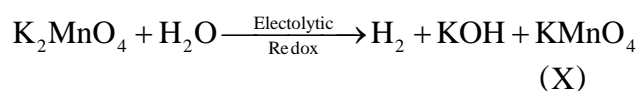
4. (C)                      5. (A)                      6. (B)                      7. (A)  
8. (B)                      9. (B)                      10. (B)                      11. (A)  
12. (A)                      13. (A)                      14. (A)

**MULTIPLE CHOICE QUESTIONS WITH ONE OR MORE THAN ONE CORRECT ANSWER :**

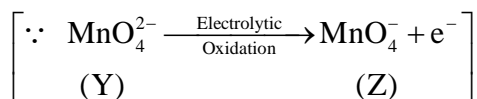
15. (B, C)                      16. (A)                      17. (A), (B), (C)  
18. Ans.(2,3,4)



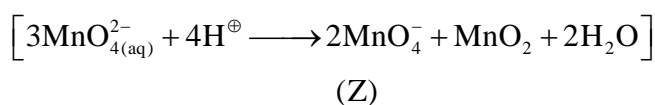




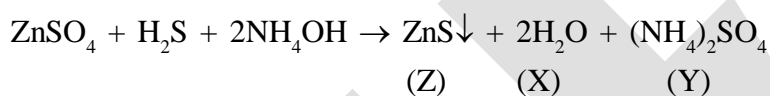
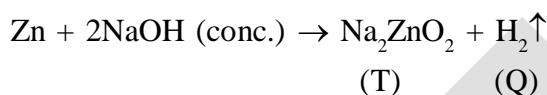
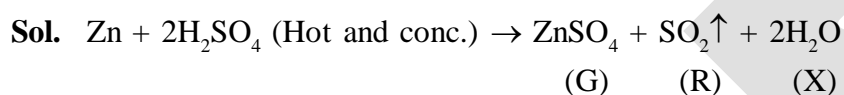
[anion of X =  $\text{MnO}_4^-$ ]  
(Z)



$\therefore$  In acidic solution; Y undergoes disproportionation reaction



19. Ans.(2,3,4)



# Important Notes

## p-BLOCK ELEMENT

### GROUP 13 ELEMENTS: THE BORON FAMILY :

Boron is a typical non-metal, aluminium is a metal but shows many chemical similarities to boron, and gallium, indium and thallium are almost exclusively metallic in character.

#### OCCURANCE

**Boron :** Boron is a fairly rare element, mainly occurs as orthoboric acid,  $(\text{H}_3\text{BO}_3)$ , borax,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ , and kernite,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ . There are two isotopic forms of boron  $^{10}\text{B}$  (19%) and  $^{11}\text{B}$  (81%).

#### ALUMINIUM :

Aluminium is the most abundant metal and the third most abundant element in the earth's crust (8.3% by mass) after oxygen (45.5%) and Si (27.7%). Bauxite,  $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$  and cryolite,  $\text{Na}_3\text{AlF}_6$  are the important minerals of aluminium.

#### ELECTRONIC CONFIGURATION :

The outer electronic configuration of these elements is  $ns^2np^1$ . A close look at the electronic configuration suggests that while boron and aluminium have noble gas core, gallium and indium have noble gas plus 10  $d$ -electrons, and thallium has noble gas plus 14  $f$ -electrons plus 10  $d$ -electron cores. Thus, the electronic structures of these elements are more complex than for the first two groups of elements discussed in unit 10. This difference in electronic structures affects the other properties and consequently the chemistry of all the elements of this group.

#### ATOMIC RADII :

On moving down the group, for each successive member one extra shell of electrons is added and, therefore, atomic radius is expected to increase. However, a deviation can be seen.

##### Atomic radii order

$\text{B} < \text{Ga} < \text{Al} < \text{In} < \text{Tl}$

##### Ionic Radii order (+3 OS)

$\text{B} < \text{Al} < \text{Ga} < \text{In} < \text{Tl}$

Atomic radius of Ga is less than that of Al. This can be understood from the variation in the inner core of the electronic configuration. The presence of additional 10  $d$ -electrons offer only poor screening effect for the outer electrons from the increased nuclear charge in gallium. Consequently, the atomic radius of gallium (135 pm) is less than that of aluminium (143 pm).

#### Ionization Enthalpy

The ionisation enthalpy values as expected from the general trends do not decrease smoothly down the group.

##### Ionization Enthalpies order

$\text{B} > \text{Tl} > \text{Ga} > \text{Al} > \text{In}$

The decrease from B to Al is associated with increase in size. The observed discontinuity in the ionisation enthalpy values between Al and Ga, and between In and Tl are due to inability of  $d$  and  $f$ -electrons, which have low screening effect, to compensate the increase in nuclear charge.

The order of ionisation enthalpies, as expected, is  $\Delta_i H_1 < \Delta_i H_2 < \Delta_i H_3$ . The sum of the first three ionisation enthalpies for each of the elements is very high. Effect of this will be apparent during study their chemical properties.

**Electronegativity**

Down the group, electronegativity first decreases from B to Al and then increases marginally. This is because of the discrepancies in atomic size of the elements.

**Physical Properties**

- (i) Boron is non-metallic in nature. It is extremely hard and black coloured solid. It exists in many allotropic forms. Due to very strong crystalline lattice, boron has unusually high melting point.
- (ii) Rest of the members are soft metals with low melting point and high electrical conductivity.
- (iii) It is worth while to note that gallium with unusually low melting point (303K), could exist in liquid state during summer. Its high boiling point (2676 K) makes it a useful material for measuring high temperatures.
- (iv) Density of the elements increases down the group from boron to thallium.

**Melting and Boiling points order**

**M.P.**  $B > Al > Tl > In > Ga$

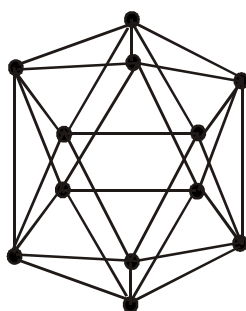
**B.P.**  $B > Al > Ga > In > Tl$

**Electropositive Character**

Due to high IE they are less electropositive on moving down the group metallic character increases due to decrease in IE [  $\therefore$  B is nonmetals and other elements are metals.]

|       |     |      |     |      |     |      |     |      |
|-------|-----|------|-----|------|-----|------|-----|------|
| $B$   | $<$ | $Al$ | $>$ | $Ga$ | $>$ | $In$ | $>$ | $Tl$ |
| Non   |     |      |     |      |     |      |     |      |
| metal |     |      |     |      |     |      |     |      |
|       |     |      |     |      |     |      |     |      |
|       |     |      |     |      |     |      |     |      |

**Note :** Boron exists in many allotropic forms. All the allotropes have basic building  $B_{12}$  icosahedral units made up of polyhedron having 20 faces and 12 corners. For example one is the simplest form :  $\alpha$  - rhombohedral boron.

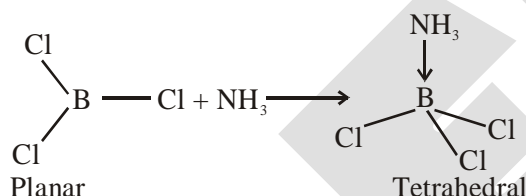


But Al, In & Tl all have close packed metal structure.

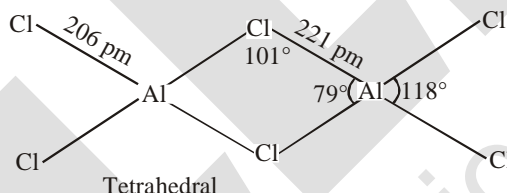
**Chemical Properties*****Oxidation state and trends in chemical reactivity***

- (i) Due to small size of boron, the sum of its first three ionization enthalpies is very high. This prevents it to form +3 ions and forces it to form only covalent compounds. But as we move from B to Al, the sum of the first three ionisation enthalpies of Al considerably decreases, and is therefore able to form  $Al^{3+}$  ions. In fact, aluminium is a highly electropositive metal.

- (ii) However, down the group, due to poor shielding effect of intervening d and f orbitals, the increased effective nuclear charge holds ns electrons tightly (responsible for inert pair effect) and thereby, restricting their participation in bonding. As a result of this, only p-orbital electrons may be involved in bonding. In fact in Ga, In and Tl, both +1 and +3 oxidation states are observed. The relative stability of +1 oxidation state progressively increases for heavier elements:  $\text{Al} < \text{Ga} < \text{In} < \text{Tl}$ . In thallium +1 oxidation state is predominant whereas the +3 oxidation state is highly oxidising in character.
- (iii) The compounds in +1 oxidation state, as expected from energy considerations, are more ionic than those in +3 oxidation state.
- (iv) In trivalent state, the number of electrons around the central atom in a molecule of the compounds of these elements (e.g., boron in  $\text{BF}_3$ ) will be only six. Such **electron deficient** molecules have tendency to accept a pair of electrons to achieve stable electronic configuration and thus, behave as Lewis acids. The tendency to behave as Lewis acid decreases with the increase in the size down the group.  $\text{BCl}_3$  easily accepts a lone pair of electrons from ammonia to form  $\text{BCl}_3 \cdot \text{NH}_3$ .



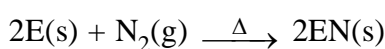
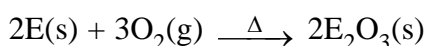
$\text{AlCl}_3$  achieves stability by forming a dimer



- (v) In trivalent state most of the compounds being covalent are hydrolysed in water. For example, the trichlorides on hydrolysis in water form tetrahedral  $[\text{M}(\text{OH})_4]^-$  species; the hybridisation state of element M is  $\text{sp}^3$ . Aluminium chloride in acidified aqueous solution forms octahedral  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  ion. In this complex ion, the 3d orbitals of Al are involved and the hybridisation state of Al is  $\text{sp}^3\text{d}^2$ .

#### REACTIVITY TOWARDS AIR :

- (i) Boron is unreactive in crystalline form.
- (ii) Aluminium forms a very thin oxide layer on the surface which protects the metal from further attack.
- (iii) Amorphous boron and aluminium metal on heating in air form  $\text{B}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  respectively. With dinitrogen at high temperature they form nitrides.



(E = element)

The nature of these oxides varies down the group. Boron trioxide is acidic and reacts with basic (metallic) oxides forming metal borates. Aluminium and gallium oxides are amphoteric and those of indium and thallium are basic in their properties.

**Reaction with Air at Water**

Al should react air to form a very thin oxide film ( $10^{-4}$  to  $10^{-6}$  mm thick) on the surface and protects the metal from further attack

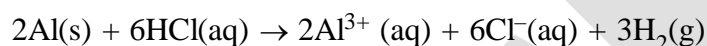


Ga and In are attacked neither by cold water nor hot water unless oxygen is present. Tl form an oxide on surface.

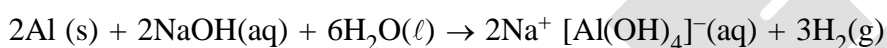
**REACTIVITY TOWARDS ACIDS AND ALKALIES :**

Boron does not react with acids and alkalies even at moderate temperature; but aluminium dissolves in mineral acids and aqueous alkalies and thus shows amphoteric character.

Aluminium dissolves in dilute HCl and liberates dihydrogen.



However, concentrated nitric acid renders aluminium passive by forming a protective oxide layer on the surface. Aluminium also reacts with aqueous alkali and liberates dihydrogen.



Sodium tetrahydroxoaluminate(III)

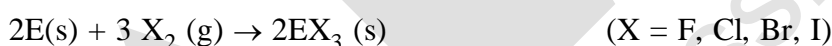
or



Ga, In, Tl dissolve in dilute acids liberating  $\text{H}_2$ . Ga is amphoteric like Al and it dissolves in aq. NaOH liberating  $\text{H}_2$  and forming gallates.

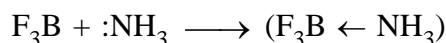
**Reactivity towards halogens :**

These elements react with halogens to form trihalides (except  $\text{TlI}_3$ ).

**IMPORTANT TRENDS AND ANOMALOUS PROPERTIES OF BORON**

Certain important trends can be observed in the chemical behaviour of group 13 elements. The tri-chlorides, bromides and iodides of all these elements being covalent in nature are hydrolysed in water. Species like tetrahedral  $[\text{M}(\text{OH})_4]^{-}$  and octahedral  $[\text{M}(\text{H}_2\text{O})_6]^{3+}$ , except in boron, exist in aqueous medium.

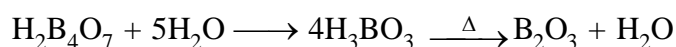
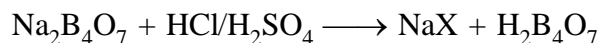
The monomeric trihalides, being electron deficient, are strong Lewis acids. Boron trifluoride easily reacts with Lewis bases such as  $\text{NH}_3$  to complete octet around boron.



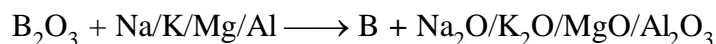
It is due to the absence of  $d$  orbitals that the maximum covalence of B is 4. Since the  $d$  orbitals are available with Al and other elements, the maximum covalence can be expected beyond 4. Most of the other metal halides (*e.g.*,  $\text{AlCl}_3$ ) are dimerised through halogen bridging (*e.g.*,  $\text{Al}_2\text{Cl}_6$ ). The metal species completes its octet by accepting electrons from halogen in these halogen bridged molecules.

**Preparation of Boron :**

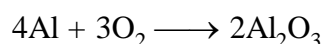
- (i) Preparation of
- $B_2O_3$
- from Borax or Colemanite



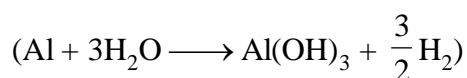
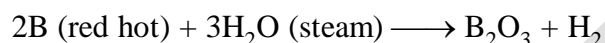
- (ii) Reduction of
- $B_2O_3$

**Chemical Properties :**

- (i) Burning in air :
- $4B + 3O_2 \longrightarrow 2B_2O_3$

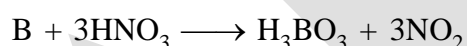
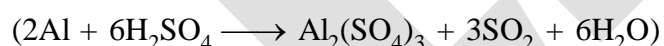
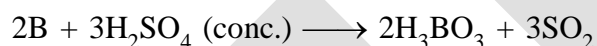
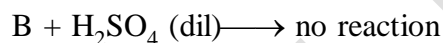


- (ii) Reaction with water



(red hot)

- (iii)
- $B + HCl \longrightarrow$
- no reaction



- (iv)
- $2B + 2NaOH + 2H_2O \xrightarrow{\Delta} 2NaBO_2 + 3H_2$



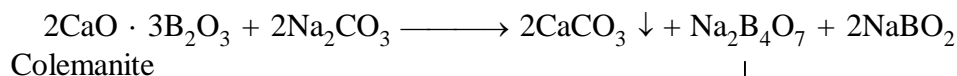
- (v)
- $2B + N_2 \longrightarrow 2BN$
- $(2Al + N_2 \longrightarrow 2AlN)$



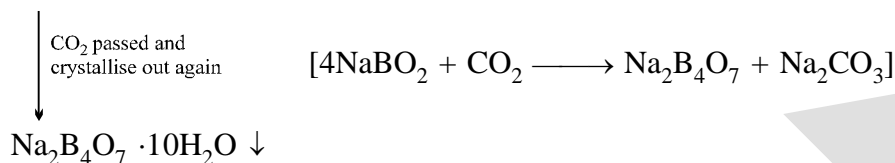
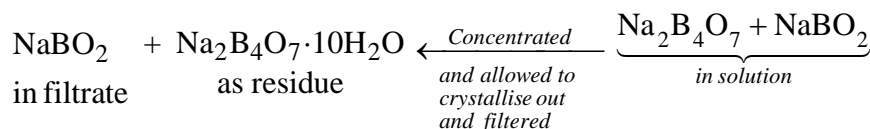
- (vi)
- $3Mg + 2B \longrightarrow Mg_3B_2$

**SOME IMPORTANT COMPOUNDS OF BORON**

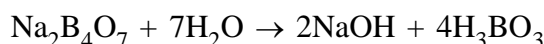
Some useful compounds of boron are borax, orthoboric acid and diborane. We will briefly study their chemistry.

**Preparation of Borax :****Borax**

↓  
Filtered  
– CaCO<sub>3</sub> (as residue)

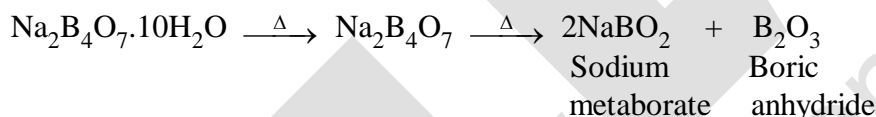
**Properties :**

- (i) It is a white crystalline solid of formula Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> · 10H<sub>2</sub>O. In fact it contains the tetranuclear units [B<sub>4</sub>O<sub>5</sub>(OH)<sub>4</sub>]<sup>2-</sup> and correct formula; therefore, is Na<sub>2</sub>[B<sub>4</sub>O<sub>5</sub>(OH)<sub>4</sub>] · 8H<sub>2</sub>O.
- (ii) Borax dissolves in water to give an alkaline solution.



Orthoboric acid

- (iii) On heating, borax first loses water molecules and swells up. On further heating it turns into a transparent liquid, which solidifies into glass like material known as borax bead.



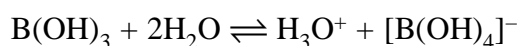
The metaborates of many transition metals have characteristic colours and, therefore, borax bead test can be used to identify them in the laboratory. For example, when borax is heated in a Bunsen burner flame with CoO on a loop of platinum wire, a blue coloured Co(BO<sub>2</sub>)<sub>2</sub> bead is formed.

**Orthoboric acid :****Preparation :**

- (i) It can be prepared by acidifying an aqueous solution of borax.
- $$\text{Na}_2\text{B}_4\text{O}_7 + 2\text{HCl} + 5\text{H}_2\text{O} \rightarrow 2\text{NaCl} + 4\text{B(OH)}_3$$
- (ii) It is also formed by the hydrolysis (reaction with water or dilute acid) of most boron compounds (halides, hydrides, etc.)

**Property :**

- (i) Orthoboric acid, H<sub>3</sub>BO<sub>3</sub> is a white crystalline solid, with soapy touch.
- (ii) It is sparingly soluble in water but highly soluble in hot water.
- (iii) H<sub>3</sub>BO<sub>3</sub> is soluble in water and behaves as weak monobasic acid. It does not donate protons like most the acids, but rather it accepts OH<sup>-</sup>. It therefore is Lewis acid (B(OH)<sub>3</sub>)

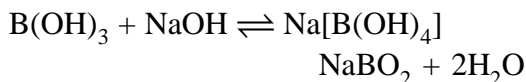


or

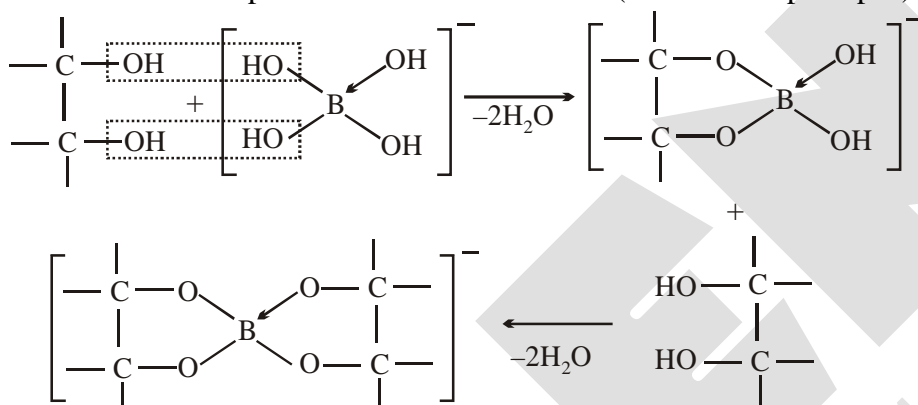




Since  $B(OH)_3$  only partially reacts with water to form  $H_3O^+$  and  $[B(OH)_4]^-$  it behaves as a weak acid. Thus it cannot be titrated satisfactorily with NaOH as a sharp end point is not obtained. If certain polyhydroxy compounds such as glycerol, mannitol or sugar are added to the titration mixture then  $B(OH)_3$  behaves as a strong monobasic acid. and hence can now be titrated with NaOH and end point is diluted using phenolphthalein as indicator.

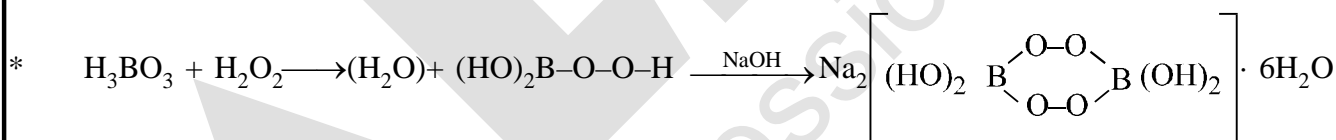
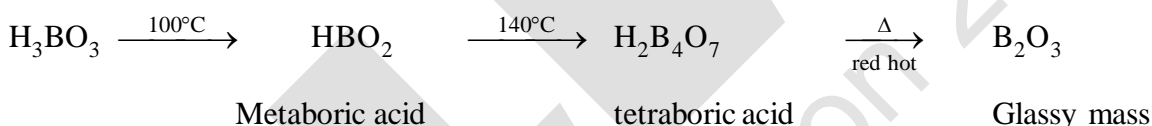


The added compound must be a cis diol to enhance the acidic proprieties in this way the cis-diol forms very stable complexes with  $[B(OH)_4]^-$  formed in forward direction above, thus effectively removing it from solution. Hence reaction proceeds in forward direction (Le-Chatelier principle.)



On heating, orthoboric acid above 370K forms metaboric acid,  $HBO_2$  which on further heating yields boric oxide,  $B_2O_3$ .

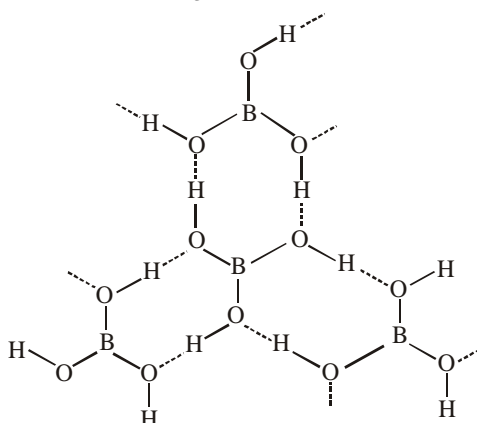
#### Heating of boric acid :



Sodium peroxy borate used in washing powder as brightner

#### STRUCTURE

It has a layer structure in which planar  $BO_3$  units are joined by hydrogen bonds as shown in figure.



Structure of boric acid; the dotted lines represent hydrogen bonds

### **Uses of boric acid :**

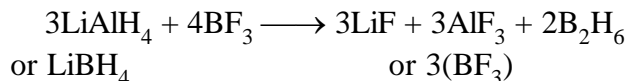
- (i) Boric acid is used in manufacturing of optical glasses
- (ii) With borax, it is used in the preparation of a buffer solution.

❑ **Diborane,  $B_2H_6$**

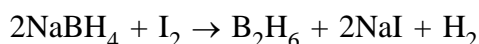
The simplest boron hydride known, is diborane.

### Preparation :

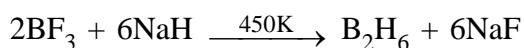
- (i) It is prepared by treating boron trifluoride with  $\text{LiAlH}_4$  in diethyl ether.



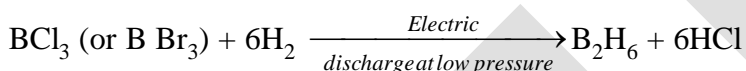
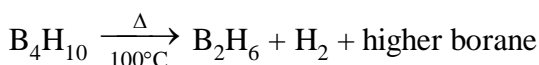
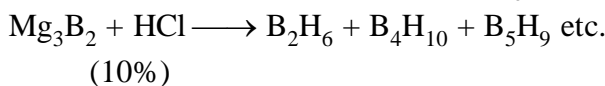
- (ii) **Laboratory method** : For the preparation of diborane involves the oxidation of sodium borohydride with iodine.



- (iii) **Industrial scale** : By the reaction of  $\text{BF}_3$  with sodium hydride.

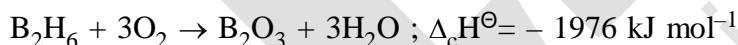


### Other reaction of preparation of $B_2H_6$ :



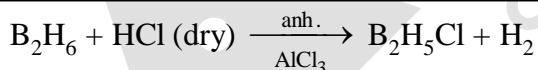
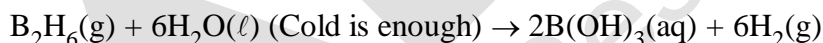
### Properties :

- (i) Diborane is a colourless, highly toxic gas with a b.p. of 180 K.
- (ii) Diborane catches fire spontaneously upon exposure to air.
- (iii) It burns in oxygen releasing an enormous amount of energy.

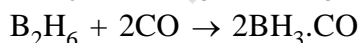
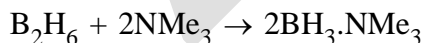


Most of the higher boranes are also spontaneously flammable in air.

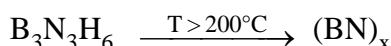
- (iv) Boranes are readily hydrolysed by water to give boric acid.



- (v) Diborane undergoes cleavage reactions with Lewis bases(L) to give borane adducts,  $\text{BH}_3 \cdot \text{L}$

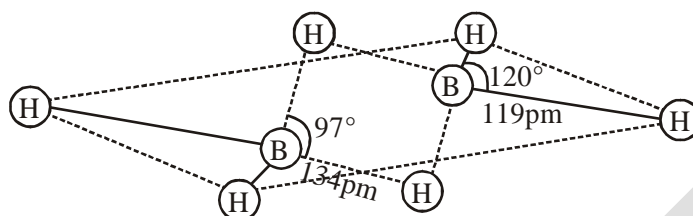


Reaction of ammonia with diborane gives initially  $\text{B}_2\text{H}_6 \cdot 2\text{NH}_3$  which is formulated as  $[\text{BH}_2(\text{NH}_3)_2]^+ [\text{BH}_4]^-$ ; further heating gives borazine,  $\text{B}_3\text{N}_3\text{H}_6$  known as “inorganic benzene” in view of its ring structure with alternate BH and NH groups.

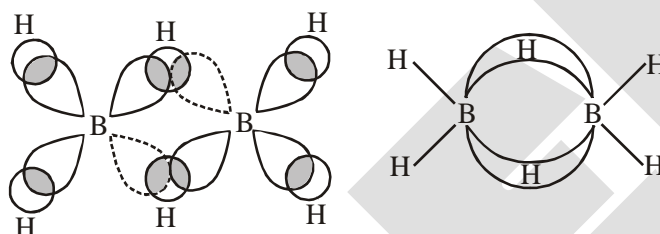


**Structure & bonding in diborane :**

The structure of diborane is shown in figure. The four terminal hydrogen atoms and the two boron atoms lie in one plane. Above and below this plane, there are two bridging hydrogen atoms. The four terminal B–H bonds are regular two centre-two electron bonds while the two bridge (B–H–B) bonds are different and can be described in terms of three centre–two electron bonds shown in figure.



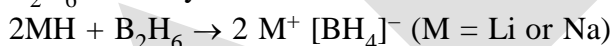
The structure of diborane,  $B_2H_6$



**Figure:** Bonding in diborane.

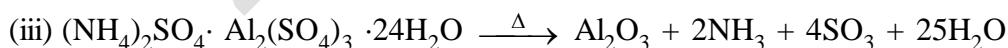
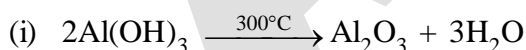
Each B atom uses  $sp^3$  hybrid orbitals for bonding. Out of the four  $sp^3$  hybrid orbital on each B atom, one is without an electron shown in broken lines. The terminal B–H bonds are normal 2-centre-2-electron bonds but the two bridge bonds are 3-centre-2-electron bonds. The 3-centre-2-electron bridge bonds are also referred to as banana bonds.

**Note: Metal hydrido borates :** Boron also forms a series of hydridoborates; the most important one is the tetrahedral  $[BH_4]^-$  ion. Tetrahydridoborates of several metals are known. Lithium and sodium tetrahydridoborates, also known as borohydrides, are prepared by the reaction of metal hydrides with  $B_2H_6$  in diethyl ether.



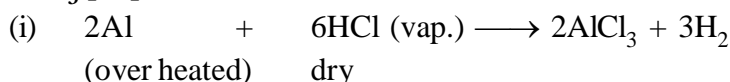
Both  $LiBH_4$  and  $NaBH_4$  are used as reducing agents in organic synthesis. They are useful starting materials for preparing other metal borohydrides.

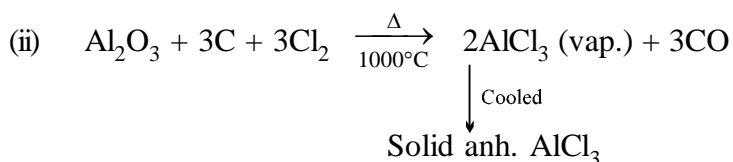
❑  **$Al_2O_3$  preparation :**



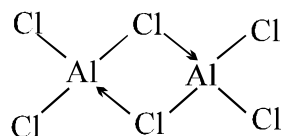
- Uses:** (i) In making refractory bricks  
 (ii) as an abrasive  
 (iii) To make high alumina cement

❑  **$AlCl_3$  preparation :**



**Properties :**

- (i) Its anhydrous form is deliquescent and fumes in air.
- (ii) It sublimes at  $180^\circ C$ .
- (iii) It is covalent and exists in the form of dimer even if in non polar solvents e.g. alcohol, ether, benzene, where it is soluble in fair extent.



- Uses:** (i) Friedel-Craft reaction  
(ii) Dyeing, drug & perfumes etc.

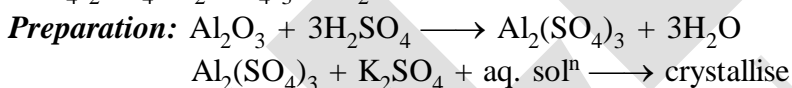
□ **Alums :**  $M_2SO_4 \cdot M'_2(SO_4)_3 \cdot 24 H_2O$

**Properties:** Swelling characteristics

where  $M = Na^+, K^+, Rb^+, Cs^+, Ag^+, Tl^+, NH_4^+$  (except  $Li^+$ )

$M' = Al^{+3}, Cr^{+3}, Fe^{+3}, Mn^{+3}, Co^{+3}$

|                                                |               |
|------------------------------------------------|---------------|
| $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$      | Potash alum   |
| $(NH_4)_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ | Ammonium alum |
| $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$      | Chrome alum   |
| $(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24H_2O$ | Ferric alum   |



- Uses:** (i) Act as coagulant  
(ii) Purification of water  
(iii) Tanning of leather  
(iv) Mordant in dyeing  
(v) Antiseptic

## USES OF BORON AND ALUMINIUM AND THEIR COMPOUNDS

### Boron :

- (i) Boron being extremely hard refractory solid of high melting point, low density and very low electrical conductivity, finds many applications.
- (ii) Boron fibres are used in making bullet-proof vest and light composite material for aircraft.
- (iii) The boron-10 ( $^{10}B$ ) isotope has high ability to absorb neutrons and, therefore, metal borides are used in nuclear industry as protective shields and control rods.
- (iv) The main industrial application of borax and boric acid is in the manufacture of heat resistant glasses(e.g., Pyrex), glass-wool and fibreglass.
- (v) Borax is also used as a flux for soldering metals, for heat, scratch and stain resistant glazed coating to earthenwares and as constituent of medicinal soaps.
- (vi) An aqueous solution of orthoboric acid is generally used as a mild antiseptic.

### Aluminium :

- (i) Aluminium is a bright silvery-white metal, with high tensile strength.
- (ii) It has a high electrical and thermal conductivity.
- (iii) On a weight-to-weight basis, the electrical conductivity of aluminium is twice that of copper.
- (iv) Aluminium is used extensively in industry and every day life.
- (v) It forms alloys with Cu, Mn, Mg, Si and Zn.
- (vi) Aluminium and its alloys can be given shapes of pipe, tubes, rods, wires, plates or foils and, therefore, find uses in packing, utensil making, construction, aeroplane and transportation industry.
- (vii) The use of aluminium and its compounds for domestic purposes is now reduced considerably because of their toxic nature.

### GROUP 14 ELEMENTS :

#### The carbon family

Carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb) are the members of group 14.

#### ❑ Occurrence of element

- (i) **Carbon** : Carbon is the seventeenth most abundant element by mass in the earth's crust. Naturally occurring carbon contains two stable isotopes:  $^{12}\text{C}$  and  $^{13}\text{C}$ . In addition to these, third isotope,  $^{14}\text{C}$  is also present. It is a radioactive isotope with half-life 5770 years and used for radiocarbon dating.
- (ii) **Silicon** : Silicon is the second (27.7 % by mass) most abundant element on the earth's crust and is present in nature in the form of silica and silicates. Silicon is a very important component of ceramics, glass and cement.
- (iii) **Germanium** : Germanium exists only in traces.
- (iv) **Tin** : Tin occurs mainly as cassiterite,  $\text{SnO}_2$
- (v) **Lead** : Lead as galena,  $\text{PbS}$ .

**Note** : Ultrapure form of germanium and silicon are used to make transistors and semiconductor devices.

#### ❑ Electronic Configuration

The valence shell electronic configuration of these elements is  $ns^2np^2$ . The inner core of the electronic configuration of elements in this group also differs.

#### ❑ Covalent Radius

There is a considerable increase in covalent radius from C to Si, thereafter from Si to Pb a small increase in radius is observed. This is due to the presence of completely filled d and f orbitals in heavier members.

Covalent radii :  $\text{C} < \text{Si} < \text{Ge} < \text{Sn} < \text{Pb}$

#### ❑ Ionization Enthalpy

The first ionization enthalpy of group 14 members is higher than the corresponding members of group 13. The influence of inner core electrons is visible here also. In general the ionisation enthalpy decreases down the group. Small decrease in  $\Delta_i H$  from Si to Ge, Ge to Sn and slight increase in  $\Delta_i H$  from Sn to Pb is the consequence of poor shielding effect of intervening d and f orbitals and increase in size of the atom.

$\text{C} > \text{Si} > \text{Ge} > \text{Pb} > \text{Sn}$  ( $\text{IE}_1$  values)

**❑ Melting and Boiling Points**M.P. :  $C > Si > Ge > Pb > Sn$ B.P. :  $Si > Ge > Sn > Pb$ **❑ Electronegativity**

Due to small size, the elements of this group are slightly more electronegative than group 13 elements. The electronegativity values for elements from Si to Pb are almost the same.

**❑ Physical Properties**

All group 14 members are solids. Carbon and silicon are non-metals, germanium is a metalloid, whereas tin and lead are soft metals with low melting points. Melting points and boiling points of group 14 elements are much higher than those of corresponding elements of group 13.

**❑ Chemical Properties*****Oxidation states and trends in chemical reactivity***

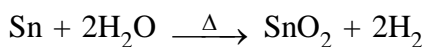
- (i) The group 14 elements have four electrons in outermost shell.
- (ii) The common oxidation states exhibited by these elements are +4 and +2. Carbon also exhibits negative oxidation states. Since the sum of the first four ionization enthalpies is very high, compounds in +4 oxidation state are generally covalent in nature.
- (iii) In heavier members the tendency to show +2 oxidation state increases in the sequence  $Ge < Sn < Pb$ . It is due to the inability of  $ns^2$  electrons of valence shell to participate in bonding. The relative stabilities of these two oxidation states vary down the group.
- (iv) Carbon and silicon mostly show +4 oxidation state.
- (v) Germanium forms stable compounds in +4 state and only few compounds in +2 state.
- (vi) Tin forms compounds in both oxidation states (Sn in +2 state is a reducing agent).
- (vii) Lead compounds in +2 state are stable and in +4 state are strong oxidising agents.
- (viii) In tetravalent state the number of electrons around the central atom in a molecule (*e.g.*, carbon in  $CCl_4$ ) is eight. Being *electron precise* molecules, they are normally not expected to act as electron acceptor or electron donor species. Although carbon cannot exceed its covalence more than 4, other elements of the group can do so. It is because of the presence of *d* orbital in them. Due to this, their halides undergo hydrolysis and have tendency to form complexes by accepting electron pairs from donor species. For example, the species like,  $SiF_6^{2-}$ ,  $[GeCl_6]^{2-}$ ,  $[Sn(OH)_6]^{2-}$  exist where the hybridisation of the central atom is  $sp^3d^2$ .

**❑ Reactivity towards oxygen**

All members when heated in oxygen form oxides. There are mainly two types of oxides, *i.e.*, monoxide and dioxide of formula  $MO$  and  $MO_2$  respectively.  $SiO$  only exists at high temperature. Oxides in higher oxidation states of elements are generally more acidic than those in lower oxidation states. The dioxides —  $CO_2$ ,  $SiO_2$  and  $GeO_2$  are acidic, whereas  $SnO_2$  and  $PbO_2$  are amphoteric in nature. Among monoxides,  $CO$  is neutral,  $GeO$  is distinctly acidic whereas  $SnO$  and  $PbO$  are amphoteric.

### ❑ Reactivity towards water

Carbon, silicon and germanium are not affected by water. Tin decomposes steam to form dioxide and dihydrogen gas.

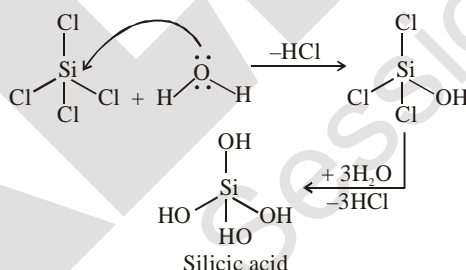


Lead is unaffected by water, probably because of a protective oxide film formation.

### ❑ Reactivity towards halogen

- These elements can form halides of formula  $\text{MX}_2$  and  $\text{MX}_4$  (where  $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ). Except carbon, all other members react directly with halogen under suitable condition to make halides.
- Most of the  $\text{MX}_4$  are covalent in nature. The central metal atom in these halides undergoes  $\text{sp}^3$  hybridisation and the molecule is tetrahedral in shape. Exceptions are  $\text{SnF}_4$  and  $\text{PbF}_4$ , which are ionic in nature.
- $\text{PbI}_4$  does not exist because  $\text{Pb—I}$  bond initially formed during the reaction does not release enough energy to unpair  $6s^2$  electrons and excite one of them to higher orbital to have four unpaired electrons around lead atom.
- Heavier members Ge to Pb are able to make halides of formula  $\text{MX}_2$ .
- Stability of dihalides increases down the group. Considering the thermal and chemical stability,  $\text{GeX}_4$  is more stable than  $\text{GeX}_2$ , whereas  $\text{PbX}_2$  is more than  $\text{PbX}_4$ .
- Except  $\text{CCl}_4$ , other tetrachlorides are easily hydrolysed by water because the central atom can accommodate the lone pair of electrons from oxygen atom of water molecule in  $d$  orbital.

Hydrolysis can be understood by taking the example of  $\text{SiCl}_4$ . It undergoes hydrolysis by initially accepting lone pair of electrons from water molecule in  $d$  orbitals of Si, finally leading to the formation of  $\text{Si(OH)}_4$  as shown below :



### IMPORTANT TRENDS AND ANOMALOUS BEHAVIOUR OF CARBON

Like first member of other groups, carbon also differs from rest of the members of its group. It is due to its smaller size, higher electronegativity, higher ionisation enthalpy unavailability of  $d$  orbitals. In carbon, only  $s$  and  $p$  orbitals are available for bonding and, therefore, it can accommodate only four pairs of electrons around it. This would limit the maximum covalence to four whereas other members can expand their covalence due to the presence of  $d$  orbitals.

Carbon also has unique ability to form  $\text{p}_\pi-\text{p}_\pi$  multiple bonds with itself and with other atoms of small size and high electronegativity. Few examples of multiple bonding are:  $\text{C}=\text{C}$ ,  $\text{C}\equiv\text{C}$ ,  $\text{C}=\text{O}$ ,  $\text{C}=\text{S}$  and  $\text{C}\equiv\text{N}$ . Heavier elements do not form  $\text{p}_\pi-\text{p}_\pi$  bonds because their atomic orbitals are too large and diffuse to have effective overlapping.

**Catenation Property**

Carbon atoms have the tendency to link with one another through covalent bonds to form chains and rings. This property is called **catenation**. This is because C—C bonds are very strong. Down the group the size increases and electronegativity decreases, and, thereby, tendency to show catenation decreases. This can be clearly seen from bond enthalpies values. The order of catenation is  $C \gg Si > Ge \approx Sn$ . Lead does not show catenation.

| Bond  | Bond enthalpy / $\text{kJ mol}^{-1}$ |
|-------|--------------------------------------|
| C—C   | 348                                  |
| Si—Si | 297                                  |
| Ge—Ge | 260                                  |
| Sn—Sn | 240                                  |

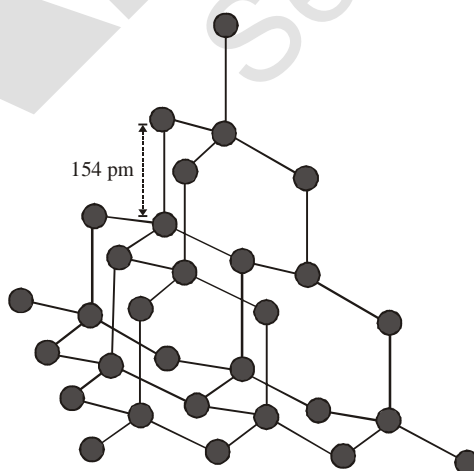
Due to property of catenation and  $p_{\pi}-p_{\pi}$  bond formation, carbon is able to show allotropic forms.

**ALLOTROPES OF CARBON**

Carbon exhibits many allotropic forms; both crystalline as well as amorphous. Diamond and graphite are two well-known crystalline forms of carbon. In 1985, third form of carbon known as **fullerenes** was discovered by H.W. Kroto, E. Smalley and R.F. Curl. For this discovery they were awarded the Nobel Prize in 1996.

**□ Diamond**

- It has a crystalline lattice.
- In diamond each carbon atom undergoes  $sp^3$  hybridisation and linked to four other carbon atoms by using hybridised orbitals in tetrahedral fashion.
- The C—C bond length is 154 pm.
- The structure extends in space and produces a rigid three-dimensional network of carbon atoms. In this



*The structure of diamond*

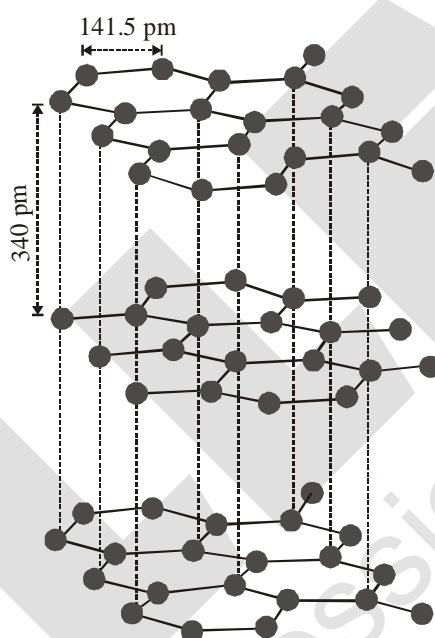


structure figure directional covalent bonds are present throughout the lattice. It is very difficult to break extended covalent bonding and, therefore, diamond is a hardest substance on the earth.

**Use :** It is used as an abrasive for sharpening hard tools, in making dyes and in the manufacture of tungsten filaments for electric light bulbs.

### □ Graphite

- (i) Graphite has layered structure figure.
- (ii) Layers are held by van der Waals forces and distance between two layers is 340 pm.
- (iii) Each layer is composed of planar hexagonal rings of carbon atoms. C—C bond length within the layer is 141.5 pm.
- (iv) Each carbon atom in hexagonal ring undergoes  $sp^2$  hybridisation and makes three sigma bonds with three neighbouring carbon atoms. Fourth electron forms a  $\pi$  bond. The electrons are delocalised over the whole sheet. Electrons are mobile and, therefore, graphite conducts electricity along the sheet.



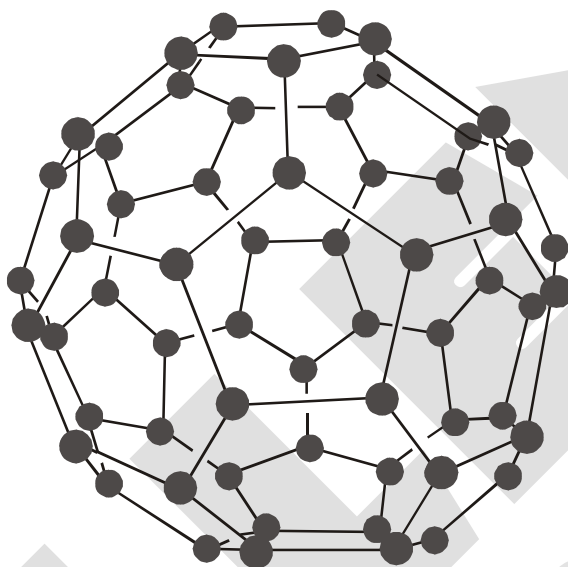
*The structure of graphite*

- (v) Graphite cleaves easily between the layers and, therefore, it is very soft and slippery. For this reason graphite is used as a dry lubricant in machines running at high temperature, where oil cannot be used as a lubricant.

### □ Fullerenes

- (i) Fullerenes are made by the heating of graphite in an electric arc in the presence of inert gases such as helium or argon. The sooty material formed by condensation of vapourised  $C^n$  small molecules consists of mainly  $C_{60}$  with smaller quantity of  $C_{70}$  and traces of fullerenes consisting of even number of carbon atoms up to 350 or above. Fullerenes are the only pure form of carbon because they have smooth structure without having 'dangling' bonds. Fullerenes are cage like molecules.  $C_{60}$  molecule has a shape like soccer ball and called **Buckminsterfullerene**.

- (ii) It contains twenty six- membered rings and twelve five membered rings.
- (iii) A six membered ring is fused with six or five membered rings but a five membered ring can only fuse with six membered rings.
- (iv) All the carbon atoms are equal and they undergo  $sp^2$  hybridisation. Each carbon atom forms three sigma bonds with other three carbon atoms. The remaining electron at each carbon is delocalised in molecular orbitals, which in turn give aromatic character to molecule.
- (v) This ball shaped molecule has 60 vertices and each one is occupied by one carbon atom and it also contains both single and double bonds with C–C distances of 143.5 pm and 138.3 pm respectively. Spherical fullerenes are also called *bucky balls* in short.



*The structure of  $C_{60}$  Buckminsterfullerene : Note that molecule has the shape of a soccer ball (football).*

**Note:** It is very important to know that graphite is thermodynamically most stable allotrope of carbon and, therefore,  $\Delta_f H^\ominus$  of graphite is taken as zero.  $\Delta_f H^\ominus$  values of diamond and fullerene,  $C_{60}$  are 1.90 and 38.1 kJ mol<sup>-1</sup>, respectively.

**Note:** Other forms of elemental carbon like carbon black, coke, and charcoal are all impure forms of graphite or fullerenes. Carbon black is obtained by burning hydrocarbons in a limited supply of air. Charcoal and coke are obtained by heating wood or coal respectively at high temperatures in the absence of air.

#### ❑ Uses of Carbon

- (i) Graphite fibres embedded in plastic material form high strength, lightweight composites. The composites are used in products such as tennis rackets, fishing rods, aircrafts and canoes.
- (ii) Being good conductor, graphite is used for electrodes in batteries and industrial electrolysis.
- (iii) Crucibles made from graphite are inert to dilute acids and alkalies.

- (iv) Being highly porous, activated charcoal is used in adsorbing poisonous gases; also used in water filters to remove organic contaminants and in airconditioning system to control odour.
- (v) Carbon black is used as black pigment in black ink and as filler in automobile tyres.
- (vi) Coke is used as a fuel and largely as a reducing agent in metallurgy.
- (vii) Diamond is a precious stone and used in jewellery. It is measured in carats (1 carat = 200 mg).

### SOME IMPORTANT COMPOUNDS OF CARBON AND SILICON

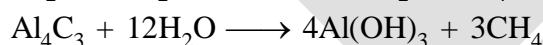
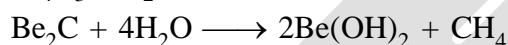
#### Types of Carbide

- (i) Ionic and salt like:

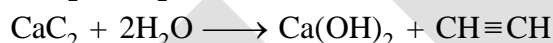
Classification on basis of  
no. of carbon atoms  
present in hydrocarbon  
found on their hydrolysis

|   |                |
|---|----------------|
| { | (a) $C_1$ unit |
|   | (b) $C_2$ unit |
|   | (c) $C_3$ unit |

**$C_1$  unit:**  $Al_4C_3, Be_2C$



**$C_2$  unit:**  $CaC_2, BaC_2$



**$C_3$  unit:**  $Mg_2C_3$



- (ii) Covalent carbide :  $SiC$  &  $B_4C$

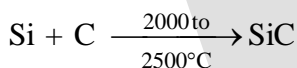
- (iii) Interstitial carbide :

(Transition element or inner transitional elements forms this kind of carbide)

Interstitial carbide formation doesn't affect the metallic lustre and electrical conductivity. ( $\because$  no chemical bond is present, no change in property)

#### **$SiC$ (Carborundum)**

#### Preparation



Note :

- (i)  $SiC$  has diamond like or wurtzite structure
- (ii)  $SiC$  is often dark purple, black or dark green due to traces of Fe and other impurities but pure sample are pale yellow to colourless.

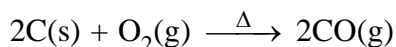
#### **Properties**

- (i) It is very hard and is used in cutting tools and abrasive powder (polishing material)
- (ii) It is very much inert
- (iii) It is not being affected by any acid except  $H_3PO_4$

### ❑ Carbon Monoxide

#### Preparation :

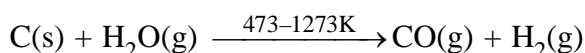
(i) Direct oxidation of C in limited supply of oxygen or air yields carbon monoxide.



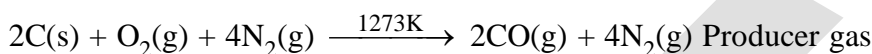
(ii) On small scale pure CO is prepared by dehydration of formic acid with concentrated  $\text{H}_2\text{SO}_4$  at 373 K



(iii) On commercial scale it is prepared by the passage of steam over hot coke. The mixture of CO and  $\text{H}_2$  thus produced is known as **water gas** or **synthesis gas**.

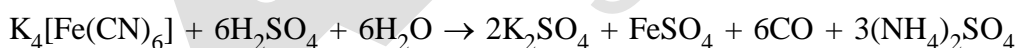
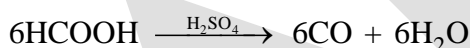
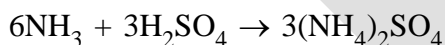
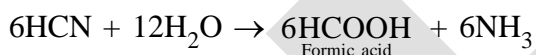
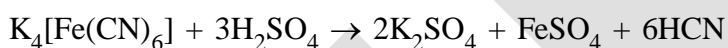


When air is used instead of steam, a mixture of CO and  $\text{N}_2$  is produced, which is called **producer gas**.



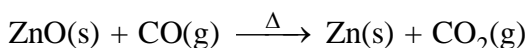
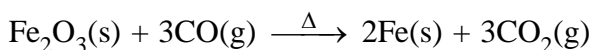
Water gas and producer gas are very important industrial fuels. Carbon monoxide in water gas or producer gas can undergo further combustion forming carbon dioxide with the liberation of heat.

**(iv) By heating potassium ferrocyanide with conc.  $\text{H}_2\text{SO}_4$  :** When potassium ferrocyanide in powdered state is heated with concentrated  $\text{H}_2\text{SO}_4$ , CO is evolved. Dilute  $\text{H}_2\text{SO}_4$  should never be used because it shall evolve highly poisonous gas HCN.



#### Properties :

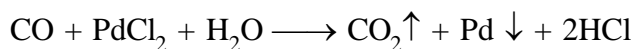
- Carbon monoxide is a colourless, odourless and almost water insoluble gas.
- It is a powerful reducing agent and reduces almost all metal oxides other than those of the alkali and alkaline earth metals, aluminium and a few transition metals. This property of CO is used in the extraction of many metals from their oxides ores.



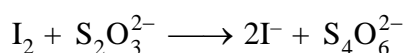
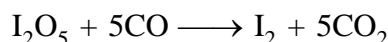
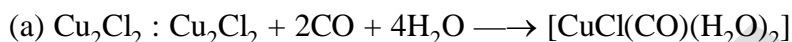
**DETECTION**

(a) burns with blue flame

(b) CO is passed through  $\text{PdCl}_2$  solution giving rise to black ppt.



Black metallic  
deposition

**ESTIMATION****ABSORBERS**

❑ **Bonding in CO mole**

In CO molecule, there are one sigma and two  $\pi$  bonds between carbon and oxygen. Because of the presence of a lone pair on carbon, CO molecule acts as a donor and reacts with certain metals when heated to form **metal carbonyls**.

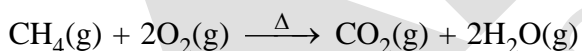
❑ **Poisonous nature of CO**

The highly poisonous nature of CO arises because of its ability to form a **complex with haemoglobin**, which is about 300 times more stable than the oxygen-haemoglobin complex. This prevents haemoglobin in the red blood corpuscles from carrying oxygen round the body and ultimately resulting in death.

❑ **Carbon Dioxide**

**Preparation :**

(i) It is prepared by complete combustion of carbon and carbon containing fuels in excess of air.



(ii) **Laboratory** by the action of dilute HCl on calcium carbonate.



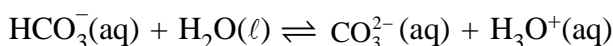
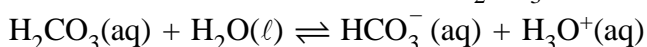
(iii) Commercial scale by heating limestone.

**Properties :**

(i) It is a colourless and odourless gas.

(ii) Its low solubility in water makes it of immense biochemical and geo-chemical importance.

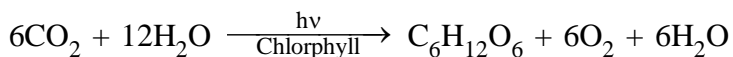
(iii) With water, it forms carbonic acid,  $\text{H}_2\text{CO}_3$  which is a weak dibasic acid and dissociates in two steps:



$\text{H}_2\text{CO}_3/\text{HCO}_3^-$  buffer system helps to maintain pH of blood between 7.26 to 7.42. Being acidic in nature, it combines with alkalis to form metal carbonates.

**Use of CO<sub>2</sub>**

Carbon dioxide, which is normally present to the extent of ~ 0.03 % by volume in the atmosphere, is removed from it by the process known as **photosynthesis**. It is the process by which green plants convert atmospheric CO<sub>2</sub> into carbohydrates such as glucose. The overall chemical change can be expressed as:

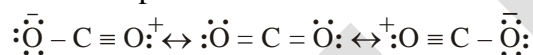


By this process plants make food for themselves as well as for animals and human beings.

**Harmful effect of CO<sub>2</sub>**

Unlike CO, it is not poisonous. But the increase in combustion of fossil fuels and decomposition of limestone for cement manufacture in recent years seem to increase the CO<sub>2</sub> content of the atmosphere. This may lead to increase in **green house effect** and thus, raise the temperature of the atmosphere which might have serious consequences.

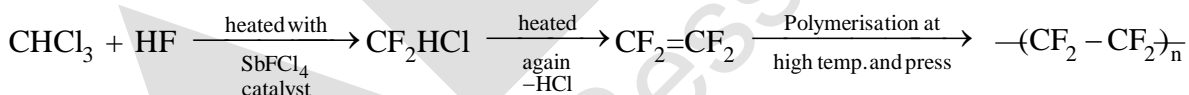
- Carbon dioxide can be obtained as a solid in the form of **dry ice** by allowing the liquified CO<sub>2</sub> to expand rapidly and dry ice is used as a refrigerant for ice-cream and frozen food.
- Gaseous CO<sub>2</sub> is extensively used to carbonate soft drinks. Being heavy and non-supporter of combustion it is used as fire extinguisher.
- A substantial amount of CO<sub>2</sub> is used to manufacture urea. In CO<sub>2</sub> molecule carbon atom undergoes *sp* hybridisation. Two *sp* hybridised orbitals of carbon atom overlap with two *p* orbitals of oxygen atoms to make two sigma bonds while other two electrons of carbon atom are involved in *p<sub>π</sub>-p<sub>π</sub>* bonding with oxygen atom. This results in its linear shape [with both C–O bonds of equal length (115 pm)] with no dipole moment. The resonance structures are shown below:



Resonating structures of carbon dioxide

**Note : Carbongene has 95% O<sub>2</sub> and 5% CO<sub>2</sub> and is used as an antidote for poisoning of CO.**

❑ **Teflon**  $-(\text{CF}_2 - \text{CF}_2)_n$



❑ **Purpose**

Temperature with standing capacity upto 300°C (1<sup>st</sup> organic compound withstand this kind of high temperature)

**SILICON (Si)**

❑ **Occurrence**

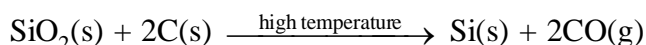
Silicon is the second most abundant (27.2%) element after oxygen (45.5%) in the earth's crust. It does not occur free in nature but in the combined state, it occurs widely in form of silica and silicates. All mineral rocks, clays and soils are built of silicates of magnesium, aluminium, potassium or iron. Aluminium silicate is however the most common constituent of rocks and clays.

Silica is found in the free state in sand, flint and quartz and in the combined state as silicates like

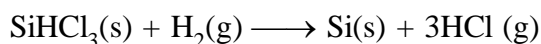
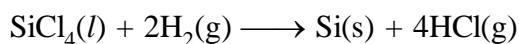
- Feldspar – K<sub>2</sub>O. Al<sub>2</sub>O<sub>3</sub>. 6SiO<sub>2</sub>
- Kaolinite – Al<sub>2</sub>O<sub>3</sub>. 2SiO<sub>2</sub>. 2H<sub>2</sub>O
- Asbestos – CaO. 3MgO. 4SiO<sub>2</sub>

**Preparation**

- (i) From silica (sand): Elemental silicon is obtained by the reduction of silica ( $\text{SiO}_2$ ) with high purity coke in an electric furnace.



- (ii) From silicon tetrachloride ( $\text{SiCl}_4$ ) or silicon chloroform ( $\text{SiHCl}_3$ ) : Silicon of very high purity required for making semiconductors is obtained by reduction of highly purified silicon tetrachloride or silicon chloroform with dihydrogen followed by purification by zone refining.



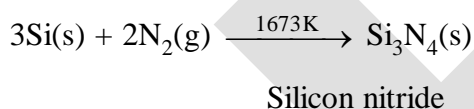
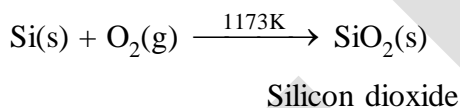
❑ **Physical Properties :**

- (i) Elemental silicon is very hard having diamond like structure.  
 (ii) It has shining luster with a melting point of 1793 K and boiling point of about 3550 K.  
 (iii) Silicon exists in three isotopes, i.e.  $^{28}_{14}\text{Si}$ ,  $^{29}_{14}\text{Si}$  and  $^{30}_{14}\text{Si}$  but  $^{28}_{14}\text{Si}$  is the most common isotope.

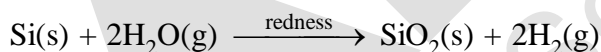
❑ **Chemical Properties :**

Silicon is particularly unreactive at room temperature towards most of the elements except fluorine. Some important chemical reactions of silicon are discussed below.

- (i) **Action of air :** Silicon reacts with oxygen of air at 1173 K to form silicon dioxide and with nitrogen of air at 1673 K to form silicon nitride,.



- (ii) **Action of steam :** It is slowly attacked by steam when heated to redness liberating dihydrogen gas.

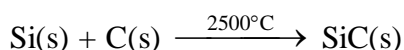


- (iii) **Reaction with halogens:** It burns spontaneously in fluorine gas at room temperature to form silicon tetrafluoride ( $\text{SiF}_4$ ).



However, with other halogens, it combines at high temperatures forming tetrahalides.

- (iv) **Reaction with carbon :** Silicon combines with carbon at 2500 °C forming silicon carbide ( $\text{SiC}$ ) known as carborundum.

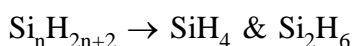


Carborundum is an extremely hard substance next only to diamond. It is mainly used as an abrasive and as a refractory material.

**Uses :**

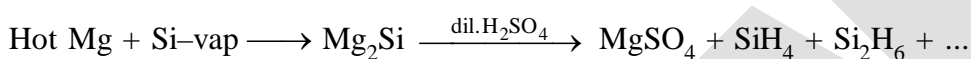
- Silicon is added to steel as such or more usually in form of ferrosilicon (an alloy of Fe and Si) to make it acid-resistant.
- High purity silicon is used as semiconductors in electronic devices such as transistors.
- It is used in the preparation of alloys such as silicon-bronze, magnesium silicon bronze and ferrosilicon.

□ **Compounds of Silicon :**

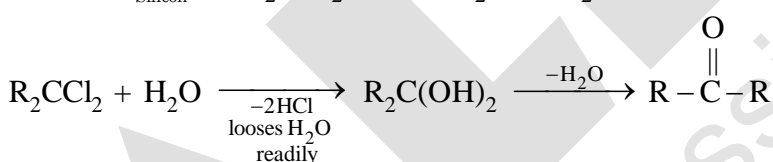
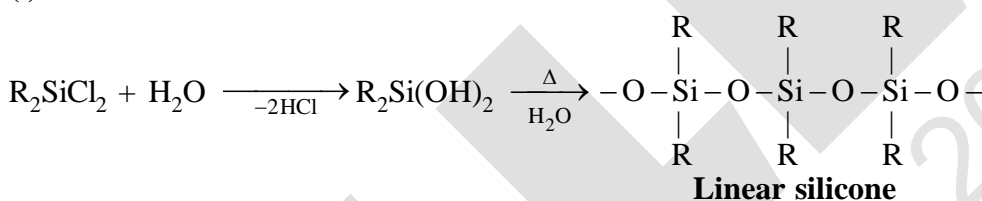
**Silane :**

Only these two are found

Higher molecules are not formed.  $\therefore$  Si can't show catenation property

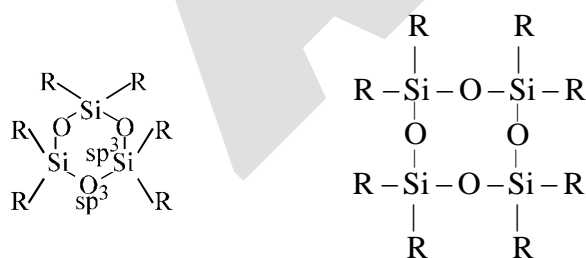
**Silicones**

It is an organosilicon polymer

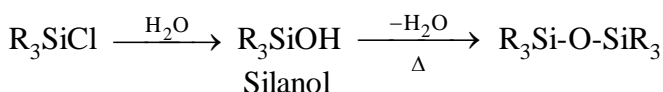
**TYPES OF SILICONES :****(i) Linear silicones****(ii) Cyclic silicones**

Silicones may have the cyclic structure also having 3, 4, 5 and 6 nos. of silicon atoms within the ring.

Alcohol analogue of silicon is known as silanol

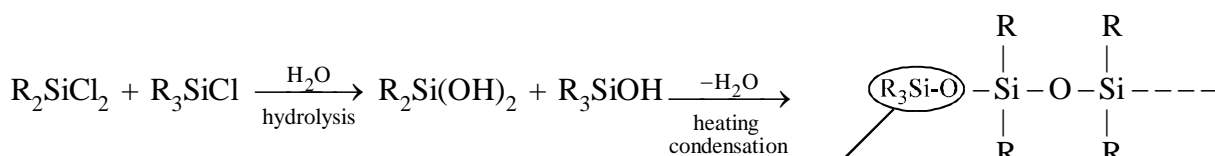


cyclic silicone not planar

**(iii) Dimer silicones**



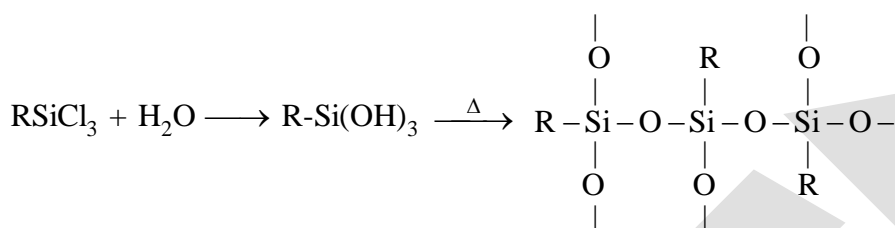
Note



This end of the chain can't be extended hence  $R_3SiCl$  is called as chain stopping unit

\* Using  $R_3SiCl$  in a certain proportion we can control the chain length of the polymer

(iv) Crossed linked silicones



cross linked silicone  
3 dimensional network

It provides the crosslinking among the chain making the polymer more hard and hence controlling the proportion of  $RSiCl_3$  we can control the hardness of polymer.

Uses

- (1) It can be used as electrical insulator (due to inertness of Si-O-Si bonds)
- (2) It is used as water repellant ( $\because$  surface is covered) eg. car polish, shoe polish, masonry works in buildings
- (3) It is used as antifoaming agent in sewage disposal, beer making and in cooking oil used to prepare potato chips.
- (4) As a lubricant in the gear boxes and light weight machinery

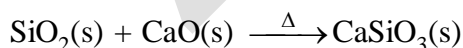
SILICA ( $SiO_2$ )

Occurrence :

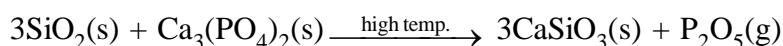
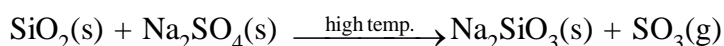
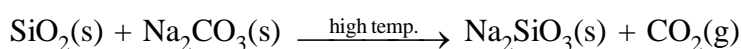
Silica or silicon dioxide occurs in nature in the free state as sand, quartz and flint and in the combined state as silicates like, Feldspar :  $K_2O \cdot Al_2O_3 \cdot 6SiO_2$ , Kaolinite :  $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$  etc.

Properties :

- (i) Pure silica is colourless, but sand is usually coloured yellow or brown due to the presence of ferric oxide as an impurity.
- (ii) Silicon dioxide is insoluble in water and all acids except hydrofluoric acid.  
 $SiO_2(s) + 4HF(l) \longrightarrow SiF_4(l) + 2H_2O(l)$
- (iii) It also combines with metallic oxides at high temperature giving silicates e.g.



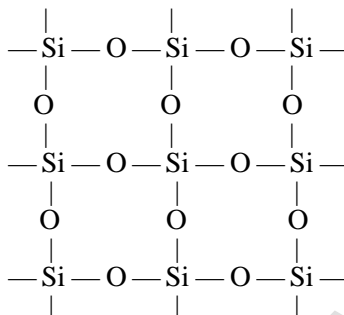
- (iv) When silica is heated strongly with metallic salts, silicates are formed and the volatile oxides are driven off as vapours.



The first two examples quoted here are important in glass making.

### Structures of Silica :

Silica has a three-dimensional network structure. In silica, silicon is  $sp^3$ -hybridized and is thus linked to four oxygen atoms and each oxygen atom is linked to two silicon atoms forming a three-dimensional giant molecule as shown in figure. This three-dimensional network structure imparts stability to  $SiO_2$  crystal and hence a large amount of energy is required to break the crystal resulting in high melting point.



### Uses :

- (i) Sand is used in large quantities to make mortar and cement.
- (ii) Being transparent to ultraviolet light, large crystal of quartz are used for making lenses for optical instruments and for controlling the frequency of radio-transmitters.
- (iii) Powdered quartz is used for making silica bricks.
- (iv) Silica gel ( $SiO_2 \cdot xH_2O$ ) is used as a desiccant (for absorbing moisture) and as an adsorbent in chromatography.

### Quartz

Quartz is extensively used as a piezoelectric material; it has made possible to develop extremely accurate clocks, modern radio and television broadcasting and mobile radio communications. Silica gel is used as a drying agent and as a support for chromatographic materials and catalysts. Kieselgur, an amorphous form of silica is used in filtration plants.

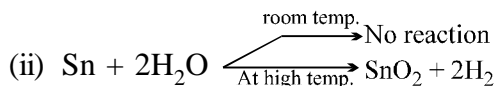
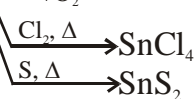
### Silicates

A large number of silicates minerals exist in nature. Some of the examples are feldspar, zeolites, mica and asbestos. Two important man-made silicates are glass and cement.

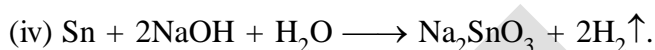
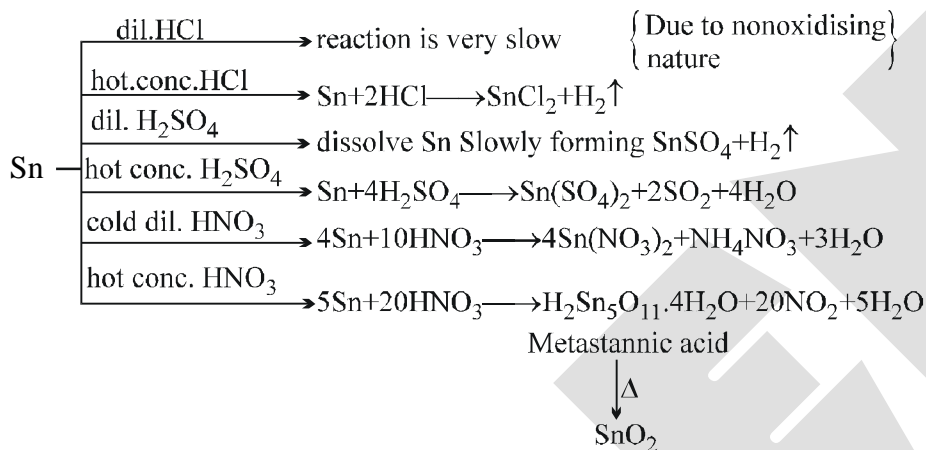
### Zeolites

If aluminium atoms replace few silicon atoms in three-dimensional network of silicon dioxide, overall structure known as aluminosilicate, acquires a negative charge. Cations such as  $Na^+$ ,  $K^+$  or  $Ca^{2+}$  balance the negative charge. Examples are feldspar and zeolites. Zeolites are widely used as a catalyst in petrochemical industries for cracking of hydrocarbons and isomerisation, e.g., ZSM-5 (A type of zeolite) used to convert alcohols directly into gasoline. Hydrated zeolites are used as ion exchangers in softening of "hard" water.

### TIN & ITS COMPOUND

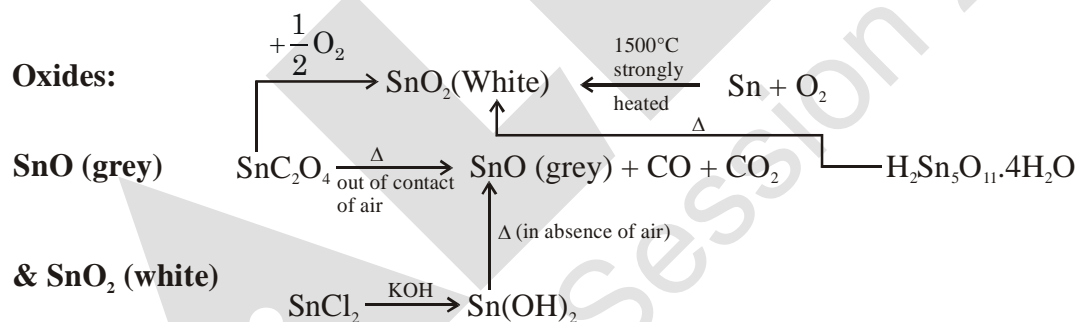


(iii) Reaction with acid.

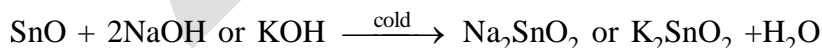
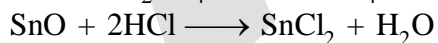


or

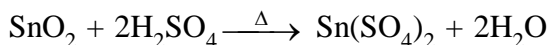
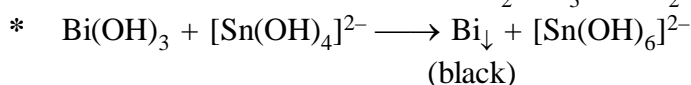
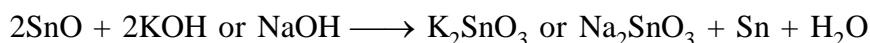
KOH [In absence of air  $\text{K}_2\text{SnO}_2$  forms and in contact with air it readily converts into  $\text{K}_2\text{SnO}_3$ ]



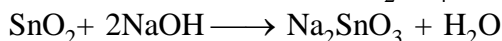
Both are amphoteric in nature :

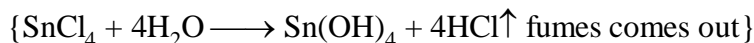
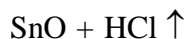
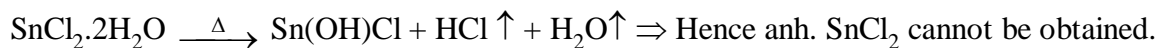
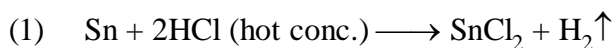


But conc. hot alkali behaves differently.

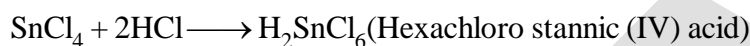
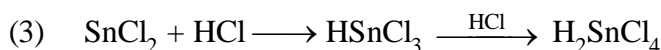
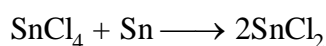


(Soluble only in hot conc.  $\text{H}_2\text{SO}_4$ )

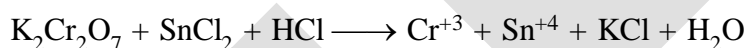
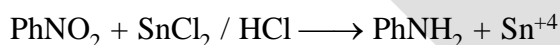
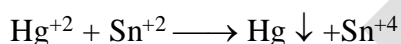
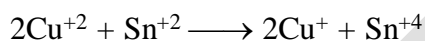
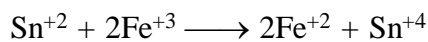


**SnCl<sub>2</sub> & SnCl<sub>4</sub> :**

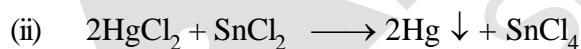
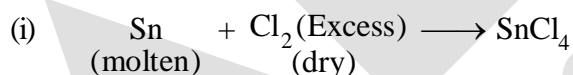
(2) A piece of Sn is always added to preserve a solution of  $\text{SnCl}_2$ . Explain.



(4) Reducing Properties of  $\text{SnCl}_2$  :



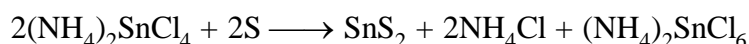
(5) Readily combines with  $\text{I}_2 \Rightarrow \text{SnCl}_2\text{I}_2 \Rightarrow$  This reaction is used to estimate tin.

**Formation of SnCl<sub>4</sub> :**

\*  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  is known as butter of tin  $\Rightarrow$  used as mordant.

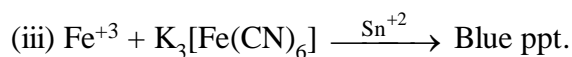
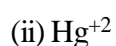
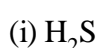
$(\text{NH}_4)_2\text{SnCl}_6$  is known as 'pink's salt'  $\Rightarrow$  used in calico printing.

**Mosaic gold :**  $\text{SnS}_2$  yellow crystalline substance :



**Note :** Mosaic gold used for filling purpose (in joining gold pieces)

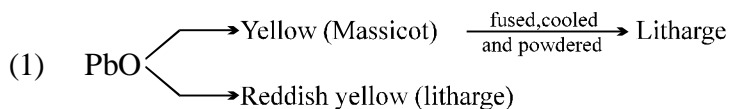
\* **Distinction of  $\text{Sn}^{+2}$  /  $\text{Sn}^{+4}$  :**



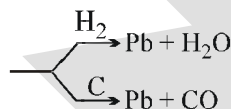
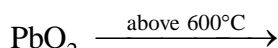
### COMPOUNDS OF LEAD

#### Oxides of lead :

- (i) PbO (ii) Pb<sub>3</sub>O<sub>4</sub> (Red)  
(iii) Pb<sub>2</sub>O<sub>3</sub> (reddish yellow) (Sesquioxide) (iv) PbO<sub>2</sub> (dark brown)



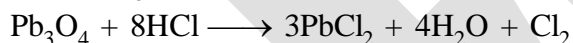
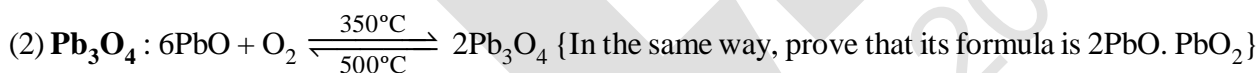
#### Laboratory Prep<sup>n</sup> :



#### Preparation of Pb<sub>2</sub>O<sub>3</sub> :

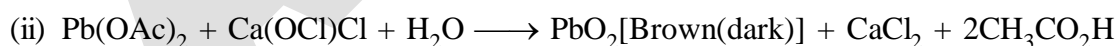
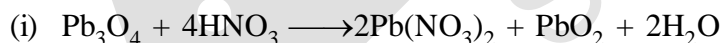


This reaction suggests that Pb<sub>2</sub>O<sub>3</sub> contains PbO<sub>2</sub>.



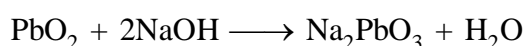
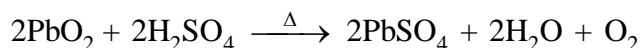
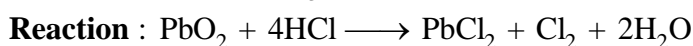
#### (3) PbO<sub>2</sub> : Insoluble in water :

HNO<sub>3</sub>, But reacts with HCl and H<sub>2</sub>SO<sub>4</sub> (hot conc.) but does not react with HNO<sub>3</sub> and soluble in hot NaOH / KOH.

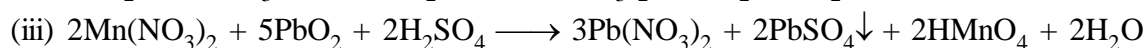
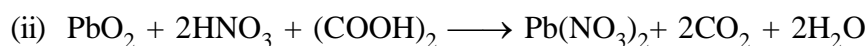
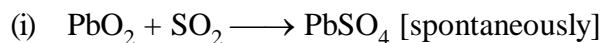


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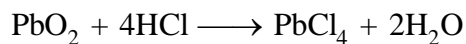
Excess bleaching powder  
is being removed by stirring with  
HNO<sub>3</sub>



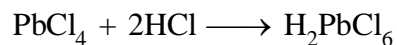
**PbO<sub>2</sub>** : Powerful oxidising agent :



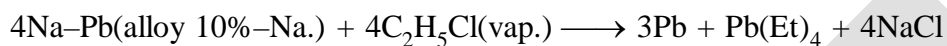
**PbCl<sub>4</sub>** : Exists as  $\text{H}_2[\text{PbCl}_6]$



{ice cold conc. saturated with  $\text{Cl}_2$ }



**TetraEthyl lead :**



It is antiknocking agent.

## NITROGEN FAMILY

## GROUP-15 ELEMENTS (N, P, As, Sb, Bi)

- (i) As we go down the group, there is a shift from non-metallic to metallic through metalloidal character.
- (ii) Nitrogen and phosphorus are **non-metals**, arsenic and antimony **metalloids** and bismuth is a **typical metal**.

**Occurrence :**

**Nitrogen :** Molecular nitrogen comprises 78% by volume of the atmosphere. It is 33<sup>rd</sup> most abundant element in the earth's crust. In the earth's crust, it occurs as sodium nitrate,  $\text{NaNO}_3$  (called Chile saltpetre) and potassium nitrate (Indian saltpetre). It is found in the form of proteins and nucleic acid in plants and animals.

**Phosphorus :**

- (i) It is eleventh most abundant element in earth's crust occurs in minerals of the apatite family,  $\text{Ca}_9(\text{PO}_4)_6 \cdot \text{CaX}_2$  ( $\text{X} = \text{F}, \text{Cl}$  or  $\text{OH}$ ) (e.g., fluorapatite  $\text{Ca}_9(\text{PO}_4)_6 \cdot \text{CaF}_2$ ) and also found as chlorapatite  $\text{Ca}_9(\text{PO}_4)_6 \cdot \text{CaCl}_2$ .
- (ii) It is also present in nucleic acid (in DNA and RNA) which are the main components of phosphate rocks.
- (iii) Arsenic, antimony and bismuth are found mainly as sulphide minerals.

**Electronic Configuration :**

The valence shell electronic configuration of these elements is  $ns^2np^3$ .

**Atomic and Ionic Radii :**

Covalent radius :  $\text{N} < \text{P} < \text{As} < \text{Sb} < \text{Bi}$

**Explanation :**

Covalent and ionic (in a particular state) radii increase in size down the group. There is a considerable increase in covalent radius from N to P. However, from As to Bi only a small increase in covalent radius is observed. This is due to the presence of completely filled d and/or f orbitals in heavier members.

**Ionisation Enthalpy :**

$\text{N} > \text{P} > \text{As} > \text{Sb} > \text{Bi}$  ( $\text{IE}_1$  values)

**Explanation :**

Ionisation enthalpy decreases down the group due to gradual increase in atomic size. Because of the extra stable half-filled p orbitals electronic configuration and smaller size, the ionisation enthalpy of the group 15 elements is much greater than that of group 14 elements in the corresponding periods. The order of successive ionisation enthalpies, as expected is  $\Delta_1 H_1 < \Delta_1 H_2 < \Delta_1 H_3$  (See above table).

**Electronegativity :**

$\text{N} > \text{P} > \text{As} > \text{Sb} = \text{Bi}$   
(1.9) (1.9)

**Explanation :**

The electronegativity value, in general, decreases down the group with increasing atomic size. However, amongst the heavier elements, the difference is not that much pronounced.

**Metallic Character**

|                                                |                                        |                                               |
|------------------------------------------------|----------------------------------------|-----------------------------------------------|
| $\frac{\text{N} < \text{P}}{\text{Non metal}}$ | $\frac{\text{As} <}{\text{Metalloid}}$ | $\frac{\text{Sb} < \text{Bi}}{\text{Metals}}$ |
|------------------------------------------------|----------------------------------------|-----------------------------------------------|

**Physical Properties :**

- All the elements of this group are polyatomic. Dinitrogen is a diatomic gas while all others are solids.
- Metallic character increases down the group.
- Nitrogen and phosphorus are non-metals, arsenic and antimony metalloids and bismuth is a metal. This is due to decrease in ionisation enthalpy and increase in atomic size.
- The boiling points, in general, increase from top to bottom in the group but the melting point increases upto arsenic and then decreases upto bismuth.
- Except nitrogen all the elements show allotropy.

P → exists in three allotropic form as white, red and black

As, Sb → exist as yellow and grey

Bi → exist as  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$  allotropic form

**Catenation**

- \* The group 15 elements also show catenation property but to much smaller extent than carbon. For example hydrazine ( $\text{H}_2\text{NNH}_2$ ) has two N atoms bonded together  $\text{HN}_3$  has three N atoms.



- \* Among group 15 elements P has the maximum tendency for catenation forming cyclic as well as open chain compounds consisting of many phosphorous atoms.

$\text{P}_2\text{H}_4$  has two P atoms bonded together the lesser tendency of elements of group 15 to show catenation in comparison to carbon is their low dissociation enthalpies.

|         |                 |
|---------|-----------------|
| C – C   | 353.3 kJ / mole |
| N – N   | 160.8 kJ / mole |
| P – P   | 201.6 kJ / mole |
| As – As | 147.4 kJ / mole |

**Chemical Properties :****Oxidation states and trends in chemical reactivity**

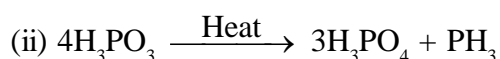
- The common oxidation states of these elements are  $-3$ ,  $+3$  and  $+5$ .
- The tendency to exhibit  $-3$  oxidation state decreases down the group due to increase in size and metallic character. Bismuth hardly forms any compound in  $-3$  oxidation state.
- The stability of  $+5$  oxidation state decreases down the group. The only well characterised Bi (V) compound is  $\text{BiF}_5$ .



- (iv) The stability of +5 oxidation state decreases and that of +3 state increases (due to inert pair effect) down the group.
- (v) Nitrogen exhibits +1, +2, +4 oxidation states also when it reacts with oxygen. Phosphorus also shows +1 and +4 oxidation states in some oxoacids.
- (vi) In the case of nitrogen, all oxidation states from +1 to +4 tend to disproportionate in acid solution. For example,



- (vii) Similarly, in case of phosphorus nearly all intermediate oxidation states disproportionate into +5 and -3 both in alkali and acid.



- (viii) +3 oxidation state in case of arsenic, antimony and bismuth becomes increasingly stable with respect to disproportionation.
- (ix) Nitrogen is restricted to a maximum covalency of 4 since only four (one s and three p) orbitals are available for bonding.
- (x) The heavier elements have vacant d orbitals in the outermost shell which can be used for bonding (covalency) and hence, expand their covalency as in  $\text{PF}_6^-$ .

### Anomalous properties of nitrogen

- (i) Nitrogen has unique ability to form  $p_\pi - p_\pi$  multiple bonds with itself and with other elements having small size and high electronegativity (e.g., C, O).
- (ii) Heavier elements of this group do not form  $p_\pi - p_\pi$  bonds as their atomic orbitals are so large and diffuse that they cannot have effective overlapping.
- (iii) Nitrogen exists as a diatomic molecule with a triple bond (one  $\sigma$  and two  $\pi$ ) between the two atoms.  $\text{N}_2$  bond enthalpy ( $941.4 \text{ kJ mol}^{-1}$ ) is very high.
- (iv) Phosphorus, arsenic and antimony form single bonds as P-P, As-As and Sb-Sb while bismuth forms metallic bonds in elemental state.
- (v) The single N-N bond is weaker than the single P-P bond because of high interelectronic repulsion of the non-bonding electrons, owing to the small bond length. As a result the catenation tendency is weaker in nitrogen.
- (vi) Another factor which affects the chemistry of nitrogen is the absence of d orbitals in its valence shell. Besides restricting its covalency to four, nitrogen cannot form  $d_\pi - p_\pi$  bond as the heavier elements can e.g.,  $\text{R}_3\text{P}=\text{O}$  or  $\text{R}_3\text{P}=\text{CH}_2$  (R=alkyl group).
- (vii) Phosphorus and arsenic can form  $d_\pi - d_\pi$  bond also with transition metals when their compounds like  $\text{P}(\text{C}_2\text{H}_5)_3$  and  $\text{As}(\text{C}_6\text{H}_5)_3$  act as ligands.

**(i) Reactivity towards hydrogen:**

All the elements of Group 15 form hydrides of the type  $\text{EH}_3$  where  $\text{E} = \text{N}, \text{P}, \text{As}, \text{Sb}$  or  $\text{Bi}$ . Some of the properties of these hydrides are shown in Table. The hydrides show regular gradation in their properties. The stability of hydrides decreases from  $\text{NH}_3$  to  $\text{BiH}_3$  which can be observed from their bond dissociation enthalpy. Consequently, the reducing character of the hydrides increases. Ammonia is only a mild reducing agent while  $\text{BiH}_3$  is the strongest reducing agent amongst all the hydrides. Basicity also decreases in the order  $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3 \geq \text{BiH}_3$ .

**Table :** Properties of Hydrides of Group 15 Elements

| Property                                                                    | $\text{NH}_3$ | $\text{PH}_3$ | $\text{AsH}_3$ | $\text{SbH}_3$ | $\text{BiH}_3$ |
|-----------------------------------------------------------------------------|---------------|---------------|----------------|----------------|----------------|
| Melting point/K                                                             | 195.2         | 139.5         | 156.7          | 185            | —              |
| Boiling point/K                                                             | 238.5         | 185.5         | 210.6          | 254.6          | 290            |
| (E–H) distance/pm                                                           | 101.7         | 141.9         | 151.9          | 170.7          | —              |
| HEH angle ( $^\circ$ )                                                      | 107.8         | 93.6          | 91.8           | 91.3           | —              |
| $\Delta_f H^\ominus / \text{kJ mol}^{-1}$                                   | – 46.1        | 13.4          | 66.4           | 145.1          | 278            |
| $\Delta_{\text{diss}} H^\ominus (\text{E} - \text{H}) / \text{kJ mol}^{-1}$ | 389           | 322           | 297            | 255            | —              |

- (ii) Reactivity towards oxygen:** All these elements form two types of oxides:  $\text{E}_2\text{O}_3$  and  $\text{E}_2\text{O}_5$ . The oxide in the higher oxidation state of the element is more acidic than that of lower oxidation state. Their acidic character decreases down the group. The oxides of the type  $\text{E}_2\text{O}_3$  of nitrogen and phosphorus are purely acidic, that of arsenic and antimony amphoteric and those of bismuth predominantly basic.
- (iii) Reactivity towards halogens:** These elements react to form two series of halides:  $\text{EX}_3$  and  $\text{EX}_5$ . Nitrogen does not form pentahalide due to non-availability of the d orbitals in its valence shell. Pentahalides are more covalent than trihalides. All the trihalides of these elements except those of nitrogen are stable. In case of nitrogen, only  $\text{NF}_3$  is known to be stable. Trihalides except  $\text{BiF}_3$  are predominantly covalent in nature.
- (iv) Reactivity towards metals:** All these elements react with metals to form their binary compounds exhibiting –3 oxidation state, such as,  $\text{Ca}_3\text{N}_2$  (calcium nitride)  $\text{Ca}_3\text{P}_2$  (calcium phosphide),  $\text{Na}_3\text{As}$  (sodium arsenide),  $\text{Zn}_3\text{Sb}_2$  (zinc antimonide) and  $\text{Mg}_3\text{Bi}_2$  (magnesium bismuthide).

**DINITROGEN****Preparation :****(a) Commercial preparation :**

Dinitrogen is produced **commercially** by the liquefaction and fractional distillation of air. Liquid dinitrogen (b.p. 77.2 K) distils out first leaving behind liquid oxygen (b.p. 90 K).

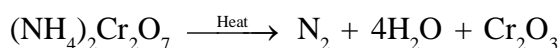
**(b) Laboratory preparation :**

(i) Dinitrogen is prepared by treating an aqueous solution of ammonium chloride with sodium nitrite.

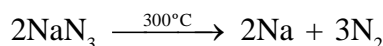
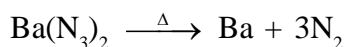


Small amounts of  $\text{NO}$  and  $\text{HNO}_3$  are also formed in this reaction; these impurities can be removed by passing the gas through aqueous sulphuric acid containing potassium dichromate.

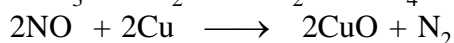
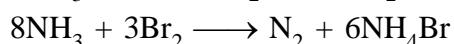
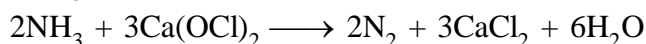
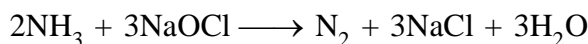
(ii) Dinitrogen can also be obtained by the thermal decomposition of ammonium dichromate.



**Note :** Very pure nitrogen can be obtained by the thermal decomposition of sodium or barium azide.

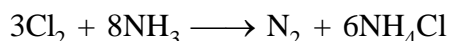
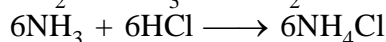
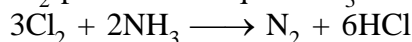


### (c) Other preparation

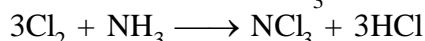


(red, overheated) (Black)

$\text{Cl}_2$  passed into liquid  $\text{NH}_3$



In this method conc. of  $\text{NH}_3$  should not be lowered down beyond a particular limit.



↓

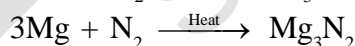
(Tremendously explosive)

### Physical properties :

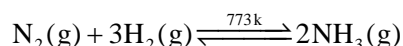
- Dinitrogen is a colourless, odourless, tasteless and non-toxic gas.
- Nitrogen atom has two stable isotopes:  $^{14}\text{N}$  and  $^{15}\text{N}$ .
- It has a very low solubility in water (23.2 cm<sup>3</sup> per litre of water at 273 K and 1 bar pressure)
- Dinitrogen has low freezing and boiling points.

### Chemical properties

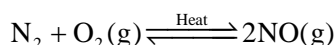
**Reaction with metal :** At higher temperatures, it directly combines with some metals to form predominantly ionic nitrides and with non-metals, covalent nitrides. A few typical reactions are:



**Reaction with metal :** It combines with hydrogen at about 773 K in the presence of a catalyst (Haber's Process) to form ammonia:

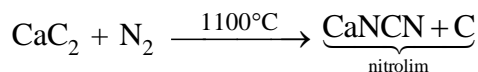


Dinitrogen combines with dioxygen only at very high temperature (at about 2000 K) to form nitric oxide, NO.

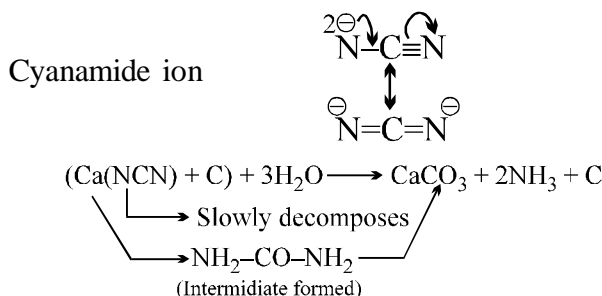


**Absorption on calcium carbide**

$N_2$  can be absorbed by calcium carbide at the temperature around  $1000^\circ\text{C}$ .



It is a very good fertiliser.

**Qus. Why dinitrogen is inert at room temperature ?**

**Ans.** Dinitrogen is inert at room temperature because of the high bond enthalpy of  $\text{N} \equiv \text{N}$  bond. Reactivity, however, increases rapidly with rise in temperature.

**TYPES OF NITRIDE :**

Salt like or ionic :  $\text{Li}_3\text{N}$ ,  $\text{Na}_3\text{N}$ ,  $\text{K}_3\text{N}$ ,  $\text{Ca}_3\text{N}_2$ ,  $\text{Mg}_3\text{N}_2$ ,  $\text{Be}_3\text{N}_2$

Covalent :  $\text{AlN}$ ,  $\text{BN}$ ,  $\text{Si}_3\text{N}_4$ ,  $\text{Ge}_3\text{N}_4$ ,  $\text{Sn}_3\text{N}_4$

Interstitial :  $\text{MN}$  ( $\text{M} = \text{Sc, Ti, Zr, Hf, La}$ )  
 HCP or FCC

No of metal atom per unit cell is equal to no of octahedral voids per unit cell.

All the octahedral voids are occupied by nitrogen atoms. Hence the formula is  $\text{MN}$ .

HCP : Hexagonal closed packing

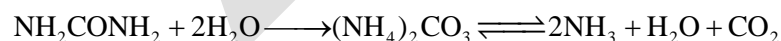
FCC : Face centred cubic

**Uses :**

- The main use of dinitrogen is in the manufacture of ammonia and other industrial chemicals containing nitrogen, (e.g., calcium cyanamide).
- It also finds use where an inert atmosphere is required (e.g., in iron and steel industry, inert diluent for reactive chemicals).
- Liquid dinitrogen is used as a refrigerant to preserve biological materials, food items and in cryosurgery.

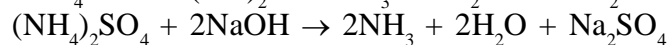
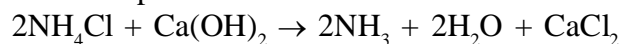
**AMMONIA****Preparation :**

(i) Ammonia is present in small quantities in air and soil where it is formed by the decay of nitrogenous organic matter e.g., urea.

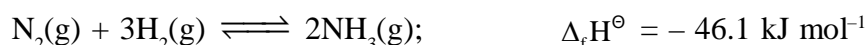


(ii) Small scale preparation

By the decomposition of ammonium salts when treated with caustic soda or calcium hydroxide.

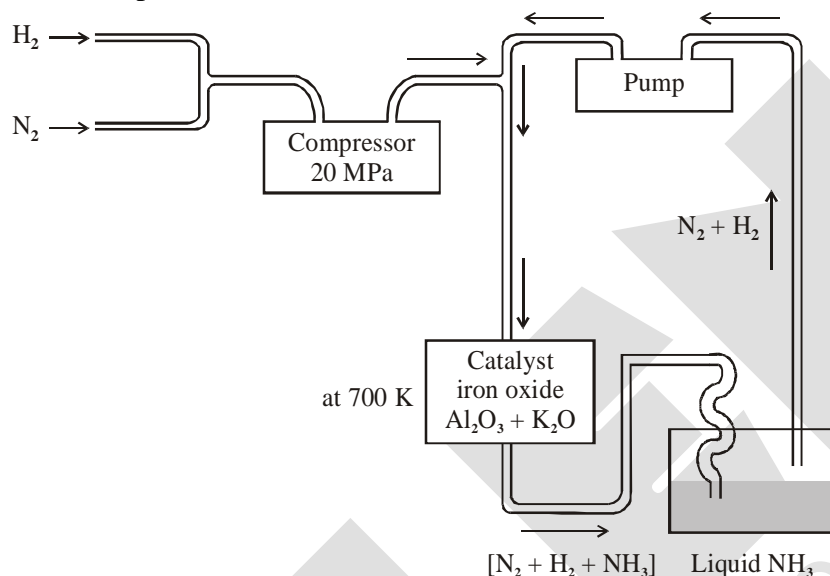


(iii) Large scale manufacturing (Haber's Process)



\* According to Le Chatelier's principle, high pressure and low temperature would favour the formation of ammonia.

- \* The optimum conditions for the production of ammonia are a pressure of  $200 \times 10^5$  Pa (about 200 atm), a temperature of  $\sim 700$  K.
- \* Use of a catalyst such as iron oxide with small amounts of  $K_2O$  and  $Al_2O_3$  to increase the rate of attainment of equilibrium.
- \* The flow chart for the production of ammonia is shown in figure. Earlier, iron was used as a catalyst with molybdenum as a promoter.



Flow chart for the manufacture of ammonia

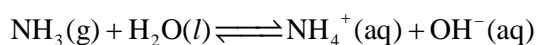
### Other preparation :

- Nitrate or nitrite reduction :  $NO_3^- / NO_2^- + Zn \text{ or } Al + NaOH \longrightarrow NH_3 + [Zn(OH)_4]^{2-} \text{ or } [Al(OH)_4]^-$
- Metal nitride hydrolysis :  $N^{3-} + 3H_2O \longrightarrow NH_3 \uparrow + 3 OH^-$

### Properties :

- Ammonia is a colourless gas with a pungent odour.
- Its freezing and boiling points are 198.4 and 239.7 K respectively.
- In the solid and liquid states, it is associated through hydrogen bonds as in the case of water and that accounts for its higher melting and boiling points than expected on the basis of its molecular mass.
- Ammonia gas is highly soluble in water.
- Basic character :**

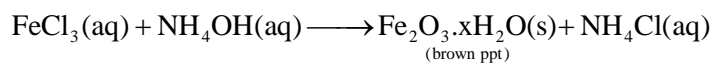
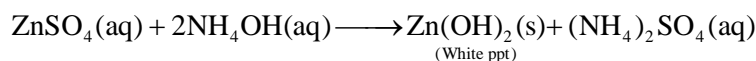
Its aqueous solution is weakly basic due to the formation of  $OH^-$  ions.



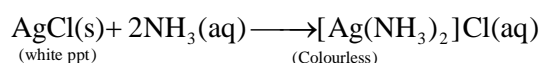
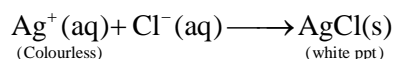
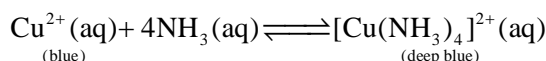
It forms ammonium salts with acids, e.g.,  $NH_4Cl$ ,  $(NH_4)_2SO_4$ , etc.

As a weak base, it precipitates the hydroxides (hydrated oxides in case of some metals) of many metals from their salt solutions.

For example,

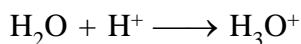
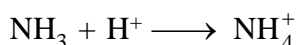
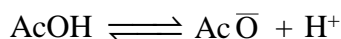


In ammonia molecule the presence of a lone pair of electrons on the nitrogen atom of the makes it a Lewis base. It donates the electron pair and forms linkage with metal ions and the formation of such complex compounds finds applications in detection of metal ions such as  $\text{Cu}^{2+}$ ,  $\text{Ag}^+$ :



### Other reactions

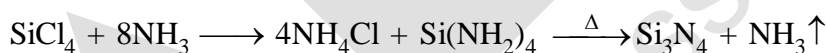
**$\text{CH}_3\text{COOH}$  is strong acid in liq.  $\text{NH}_3$  while in water is weak acid.**



Basicity order  $\text{NH}_3 > \text{H}_2\text{O}$

more solvation of  $\text{H}^+$  in  $\text{NH}_3$ .

**Hydrolysis and Ammonolysis occurs is a same way.**



Rate of hydrolysis and Ammonolysis will be affected by the presence of  $\text{HCl}$  vapour &  $\text{NH}_4\text{Cl}$  vapour respectively.

### Uses :

- (i) Ammonia is used to produce various nitrogenous fertilisers (ammonium nitrate, urea, ammonium phosphate and ammonium sulphate).
- (ii) In the manufacture of some inorganic nitrogen compounds, the most important one being nitric acid.
- (iii) Liquid ammonia is also used as a refrigerant.

### BONDING IN AMMONIA :

The ammonia molecule is trigonal pyramidal with the nitrogen atom at the apex. It has three bond pairs and one lone pair of electrons.

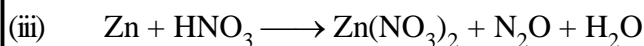
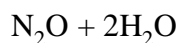
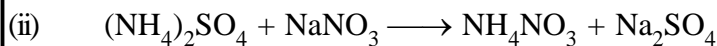
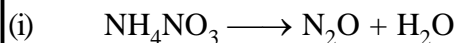
### OXIDES OF NITROGEN :

Nitrogen forms a number of oxides in different oxidation states. The names, formulas, preparation and physical appearance of these oxides are given in Table.

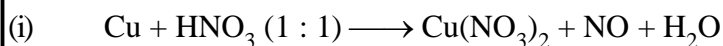
| Oxides of Nitrogen                            |                               |                             |                                                                                                                                                        |                                                                      |
|-----------------------------------------------|-------------------------------|-----------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------|
| Name                                          | Formula                       | Oxidation state of nitrogen | Common methods of preparation                                                                                                                          | Physical appearance and chemical nature                              |
| Dinitrogen oxide<br>[Nitrogen oxide]          | N <sub>2</sub> O              | +1                          | $\text{NH}_4\text{NO}_3 \xrightarrow{\text{Heat}} \text{N}_2\text{O} + 2\text{H}_2\text{O}$                                                            | Colourless gas, neutral                                              |
| Nitrogen monoxide<br>[Nitrogen (II) oxide]    | NO                            | +2                          | $2\text{NaNO}_2 + 2\text{FeSO}_4 + 3\text{H}_2\text{SO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + 2\text{NaHSO}_4 + 2\text{H}_2\text{O} + 2\text{NO}$ | Colourless gas, neutral                                              |
| Dinitrogen trioxide<br>[Nitrogen (III) oxide] | N <sub>2</sub> O <sub>3</sub> | +3                          | $2\text{NO} + \text{N}_2\text{O}_4 \xrightarrow{-30^\circ\text{C}} 2\text{N}_2\text{O}_3$                                                              | Pale Blue solid (MP = -100.1°C), acidic, Intense blue liquid (-30°C) |
| Nitrogen dioxide<br>[Nitrogen (IV) oxide]     | NO <sub>2</sub>               | +4                          | $2\text{Pb}(\text{NO}_3)_2 \xrightarrow{673\text{K}} 4\text{NO}_2 + 2\text{PbO} + \text{O}_2$                                                          | brown gas, acidic                                                    |
| Dinitrogen tetroxide<br>[Nitrogen (IV) oxide] | N <sub>2</sub> O <sub>4</sub> | +4                          | $2\text{NO}_2 \xrightleftharpoons[\text{Heat}]{\text{Cool}} \text{N}_2\text{O}_4$                                                                      | Colourless solid/liquid, acidic                                      |
| Dinitrogen pentaoxide<br>[Nitrogen(V) oxide]  | N <sub>2</sub> O <sub>5</sub> | +5                          | $4\text{HNO}_3 + \text{P}_4\text{O}_{10} \rightarrow 4\text{HPO}_3 + 2\text{N}_2\text{O}_5$                                                            | colourless solid, acidic                                             |

### Structure of Oxides of Nitrogen

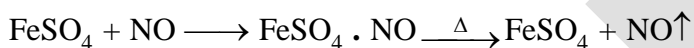
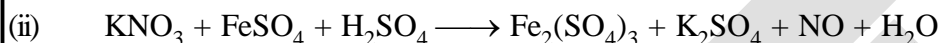
| Formula                       | Resonance structures                                                                                                                                                                                                                                                                                                            | Bond Parameters                                                                                   |
|-------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------|
| N <sub>2</sub> O              | $\ddot{\text{N}}=\text{N}=\ddot{\text{O}} \leftrightarrow \text{:}\ddot{\text{N}}\equiv\text{N}-\ddot{\text{O}}\text{:}$                                                                                                                                                                                                        | $\text{N}-\text{N}-\text{O}$<br>113 pm    119 pm<br>Linear                                        |
| NO                            | $\text{:}\ddot{\text{N}}=\ddot{\text{O}}\text{:} \leftrightarrow \text{:}\ddot{\text{N}}\equiv\ddot{\text{O}}\text{:}$                                                                                                                                                                                                          | $\text{N}-\text{O}$<br>115 pm<br>Linear                                                           |
| N <sub>2</sub> O <sub>3</sub> | $\begin{array}{c} \ddot{\text{O}} \\ \parallel \\ \text{:}\ddot{\text{N}}-\text{N}=\ddot{\text{O}} \\ \parallel \\ \ddot{\text{O}} \end{array} \leftrightarrow \begin{array}{c} \ddot{\text{O}} \\ \parallel \\ \text{:}\ddot{\text{N}}-\text{N}=\ddot{\text{O}} \\ \parallel \\ \ddot{\text{O}} \end{array}$                   | $\text{O}-\text{N}-\text{O}$<br>114 pm    105°<br>186 pm    117°<br>121 pm    130°                |
| NO <sub>2</sub>               | $\begin{array}{c} \ddot{\text{O}} \\ \parallel \\ \text{:}\ddot{\text{N}}-\ddot{\text{O}} \\ \parallel \\ \ddot{\text{O}} \end{array} \leftrightarrow \begin{array}{c} \ddot{\text{O}} \\ \parallel \\ \text{:}\ddot{\text{N}}-\ddot{\text{O}} \\ \parallel \\ \ddot{\text{O}} \end{array}$                                     | $\text{O}-\text{N}-\text{O}$<br>120 pm<br>134°<br>Angular                                         |
| N <sub>2</sub> O <sub>4</sub> | $\begin{array}{c} \ddot{\text{O}} \\ \parallel \\ \text{:}\ddot{\text{N}}-\text{N}=\ddot{\text{O}} \\ \parallel \\ \ddot{\text{O}} \end{array} \leftrightarrow \begin{array}{c} \ddot{\text{O}} \\ \parallel \\ \text{:}\ddot{\text{N}}-\text{N}=\ddot{\text{O}} \\ \parallel \\ \ddot{\text{O}} \end{array}$                   | $\text{O}-\text{N}-\text{O}$<br>135°<br>175 pm<br>Planar<br>$\text{N}-\text{O}$<br>121 pm         |
| N <sub>2</sub> O <sub>5</sub> | $\begin{array}{c} \ddot{\text{O}} \\ \parallel \\ \text{:}\ddot{\text{N}}-\text{O}-\text{N}=\ddot{\text{O}} \\ \parallel \\ \ddot{\text{O}} \end{array} \leftrightarrow \begin{array}{c} \ddot{\text{O}} \\ \parallel \\ \text{:}\ddot{\text{N}}-\text{O}-\text{N}=\ddot{\text{O}} \\ \parallel \\ \ddot{\text{O}} \end{array}$ | $\text{O}-\text{N}-\text{O}$<br>151 pm<br>112°<br>Planar<br>$\text{N}-\text{O}$<br>119 pm<br>134° |

**Preparation:**1. **N<sub>2</sub>O**

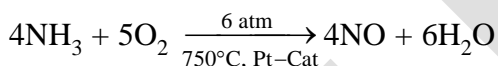
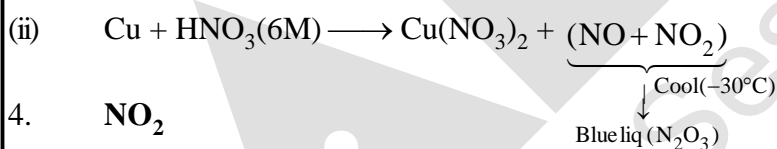
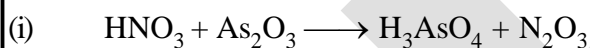
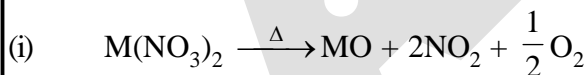
(dil. &amp; cold)

2. **NO**

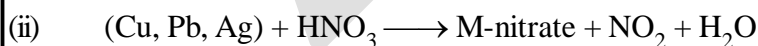
hot



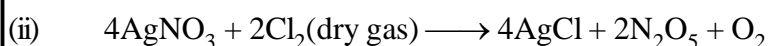
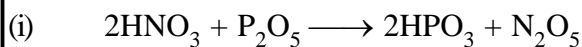
Industrial process.

3. **N<sub>2</sub>O<sub>3</sub>**4. **NO<sub>2</sub>**

M = Pb, Cu, Ba, Ca



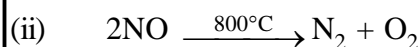
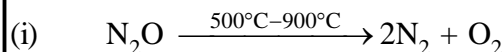
(hot &amp; conc.)

5. **N<sub>2</sub>O<sub>5</sub>**

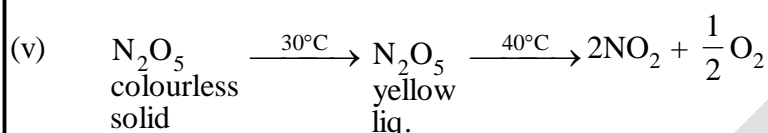
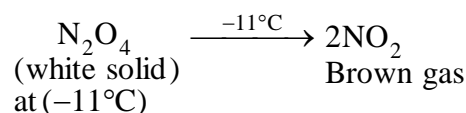
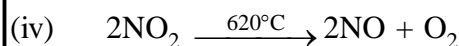


**Properties:**

**(I) Decomposition Behaviour**



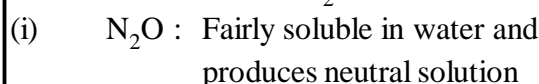
(Blue liq.) at  $(-30^\circ\text{C})$



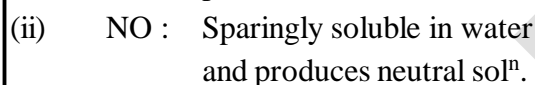
**(II) Reaction with  $\text{H}_2\text{O}$  &  $\text{NaOH}$**

$\text{H}_2\text{O}$

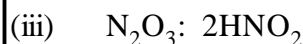
$\text{NaOH}$



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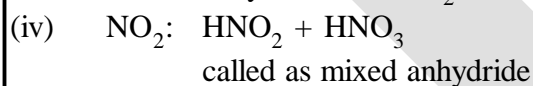


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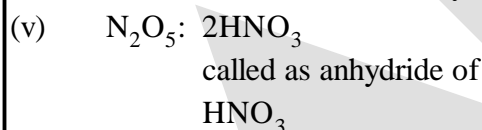


Hence it is known as anhydride of  $\text{HNO}_2$

$\text{NaNO}_2$

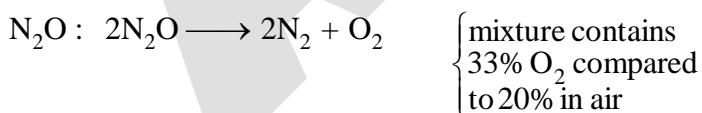


$\text{NaNO}_2 + \text{NaNO}_3$

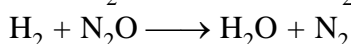
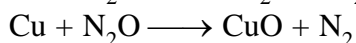
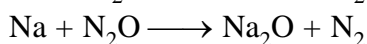
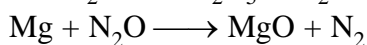
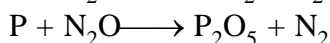
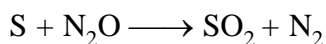


$\text{NaNO}_3$

**Other properties:**



Hence, it is a better supporter for combustion.



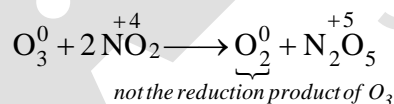
- NO : (i) It burns :  $\text{NO} + \frac{1}{2} \text{O}_2 \longrightarrow \text{NO}_2$
- (ii) It supports combustion also for molten sulphur and hot phosphorous.  
 $\text{S} + 2\text{NO} \longrightarrow \text{SO}_2 + \text{N}_2$   
 $2\text{P} + 5\text{NO} \longrightarrow \text{P}_2\text{O}_5 + \frac{5}{2} \text{N}_2$
- (iii) It is being absorbed by  $\text{FeSO}_4$  solution.
- (iv) It is having reducing property.  
 $\text{KMnO}_4 + \text{NO} + \text{H}_2\text{SO}_4 \longrightarrow \text{K}_2\text{SO}_4 + \text{MnSO}_4 + \text{HNO}_3 + \text{H}_2\text{O}$   
 $\text{HOCl} + \text{NO} + \text{H}_2\text{O} \longrightarrow \text{HNO}_3 + \text{HCl}$
- (v) NO shows oxidising property also.  
 $\text{SO}_2 + 2\text{NO} + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4 + \text{N}_2\text{O}$   
 $\text{H}_2\text{S} + 2\text{NO} \longrightarrow \text{H}_2\text{O} + \text{S} \downarrow + \text{N}_2\text{O}$   
 $3\text{SnCl}_2 + 2\text{NO} + 6\text{HCl} \longrightarrow 3\text{SnCl}_4 + 2\text{NH}_2\text{OH}$   
 (Used for  $\text{NH}_2\text{OH}$  preparation)
- (vi) NO combines with  $\text{X}_2$  ( $\text{X}_2 = \text{Cl}_2, \text{Br}_2, \text{F}_2$ ) to produce NO X  
 $2\text{NO} + \text{X}_2 \longrightarrow 2\text{NOX}$

$\text{N}_2\text{O}_3$  : No more properties.

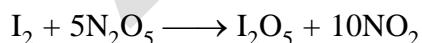
- $\text{NO}_2$  : (1) It is having oxidising property.  
 $\text{S} + \text{NO}_2 \longrightarrow \text{SO}_2 + \text{NO}$   
 $\text{P} + \text{NO}_2 \longrightarrow \text{P}_2\text{O}_5 + \text{NO}$   
 $\text{C} + \text{NO}_2 \longrightarrow \text{CO}_2 + \text{NO}$   
 $\text{SO}_2 + \text{NO}_2 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4 + \text{NO}$   
 $\text{H}_2\text{S} + \text{NO}_2 \longrightarrow \text{H}_2\text{O} + \text{S} \downarrow + \text{NO}$   
 $\text{CO} + \text{NO}_2 \longrightarrow \text{CO}_2 + \text{NO}$

NO not formed :  $2\text{KI} + 2\text{NO}_2 \longrightarrow \text{I}_2 + 2\text{KNO}_2$

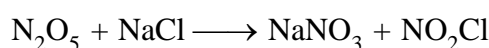
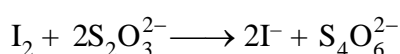
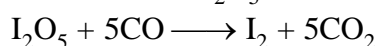
- (2) Reducing property of  $\text{NO}_2$ .  
 $\text{KMnO}_4 + \text{NO}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{K}_2\text{SO}_4 + \text{MnSO}_4 + \text{HNO}_3 + \text{H}_2\text{O}$



$\text{N}_2\text{O}_5$  :



$\text{I}_2\text{O}_5$  is used for the estimation of CO



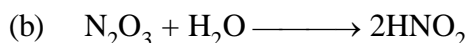
This proves that  $\text{N}_2\text{O}_5$  is consisting of ion pair of  $\text{NO}_2^+$  &  $\text{NO}_3^-$

## OXOACIDS OF NITROGEN

$\text{H}_2\text{N}_2\text{O}_2$  (hyponitrous acid),  $\text{HNO}_2$  (nitrous acid) and  $\text{HNO}_3$  (nitric acid). Amongst them  $\text{HNO}_3$  is the most important.

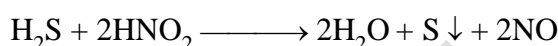
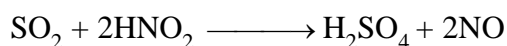
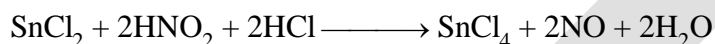
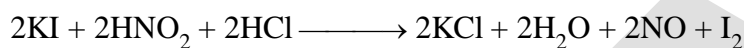
NITROUS ACID ( $\text{HNO}_2$ )

## Preparation

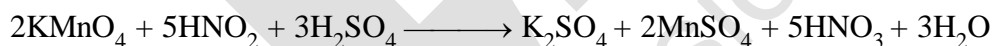
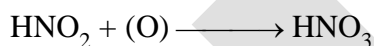


## Properties

- (a) **Oxidising property** : Because of its easy oxidation to liberate nascent oxygen, it acts as a strong oxidant  $2\text{HNO}_2 \longrightarrow \text{H}_2\text{O} + 2\text{NO} + (\text{O})$



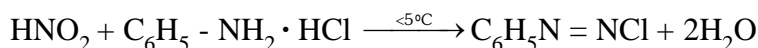
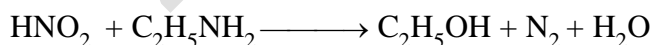
- (b) **Reducing property** : Nitrous acid also acts as a reducing agent as it can be oxidised into nitric acid.



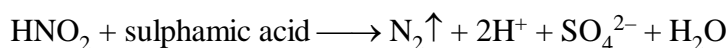
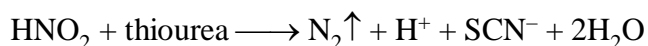
- (c) **Reaction with  $\text{NH}_3$  /  $-\text{NH}_2$  compounds :**



Urea



Benzene diazonium chloride

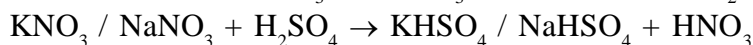


## NITRIC ACID

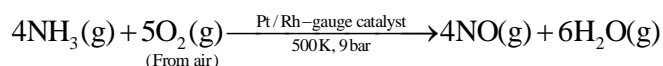
It was named aqua fortis (means strong water) by alchemists.

**Preparation :**

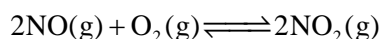
**Laboratory Method :** By heating  $\text{KNO}_3$  or  $\text{NaNO}_3$  and concentrated  $\text{H}_2\text{SO}_4$  in a glass retort.

**Large scale preparation (Ostwald's process) :**

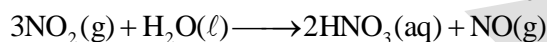
(i) This method is based upon catalytic oxidation of  $\text{NH}_3$  by atmospheric oxygen.



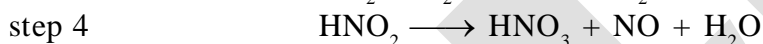
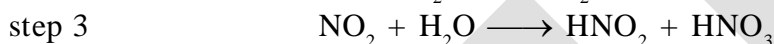
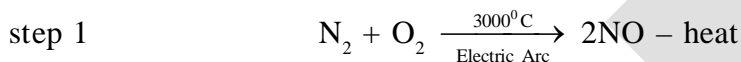
(ii) Nitric oxide thus formed combines with oxygen giving  $\text{NO}_2$ .



(iii) Nitrogen dioxide so formed, dissolves in water to give  $\text{HNO}_3$ .



$\text{NO}$  thus formed is recycled and the aqueous  $\text{HNO}_3$  can be concentrated by distillation upto ~ 68% by mass. Further concentration to 98% can be achieved by dehydration with concentrated  $\text{H}_2\text{SO}_4$ .

**Birkeland Eyde Process or arc process****Properties****Physical properties**

It has extremely corrosive action on the skin and causes painful sores.

(i) It is a colourless liquid (f.p. 231.4 K and b.p. 355.6 K).

(ii) Laboratory grade nitric acid contains ~ 68% of the  $\text{HNO}_3$  by mass and has a specific gravity of 1.504.

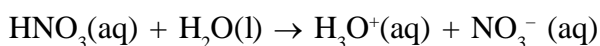
(iii) Nitric acid usually acquires yellow or brown colour due to its decomposition by sunlight into  $\text{NO}_2$ .



The yellow or brown colour of the acid can be removed by warming it to 60-80°C and bubbling dry air through it.

**Chemical properties**

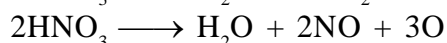
**Acidic character** in aqueous solution, nitric acid behaves as a strong acid giving hydronium and nitrate ions.



**Oxidising nature:** Nitric acid acts as a strong oxidising agent as it decomposes to give nascent oxygen easily.

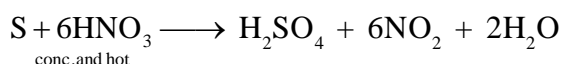


or

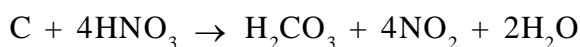


(i) **Oxidation of non-metals :** The nascent oxygen oxidises various non-metals to their corresponding oxyacids of highest oxidation state.

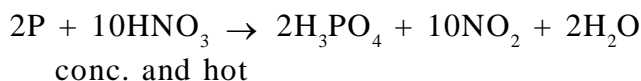
- (1) Sulphur is oxidised to sulphuric acid



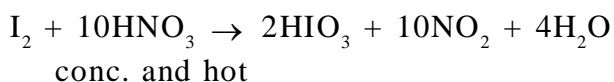
- (2) Carbon is oxidised to carbonic acid



- (3) Phosphorus is oxidised to orthophosphoric acid.



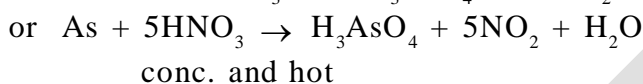
- (4) Iodine is oxidised to iodic acid



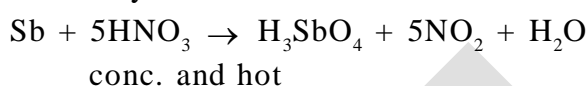
**(ii) Oxidation of metalloids**

Metalloids like non-metals also form oxyacids of highest oxidation state.

- (1) Arsenic is oxidised to arsenic acid



- (2) Antimony is oxidised to antimononic acid



- (3) Tin is oxidised to meta-stannic acid.



**(iii) Oxidation of Compounds:**

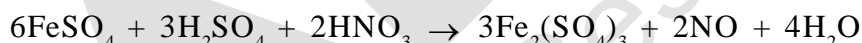
- (1) Sulphur dioxide is oxidised to sulphuric acid



- (2) Hydrogen sulphide is oxidised to sulphur



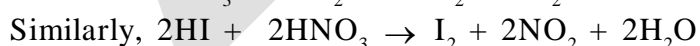
- (3) Ferrous sulphate is oxidised to ferric sulphate in presence of  $\text{H}_2\text{SO}_4$



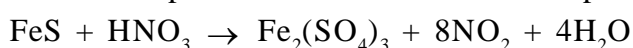
- (4) Iodine is liberated from KI.



- (5) HBr, HI are oxidised to  $\text{Br}_2$  and  $\text{I}_2$ , respectively.



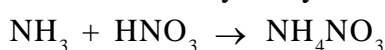
- (6) Ferrous sulphide is oxidised to ferric sulphate



- (7) Stannous chloride is oxidised to stannic chloride in presence of HCl.



Hydroxylamine



## (8) Oxidation of organic compounds .

Sawdust catches fire when nitric acid is poured on it.

Turpentine oil bursts into flames when treated with fuming nitric acid.

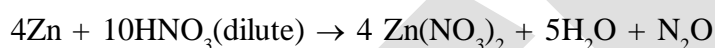
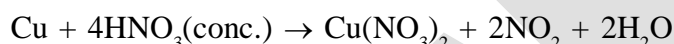
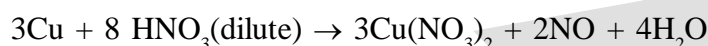
Toluene is oxidised to benzoic acid with dil.  $\text{HNO}_3$ .

Cane sugar is oxidised to oxalic acid.



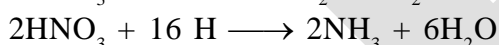
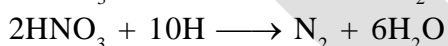
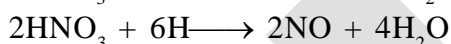
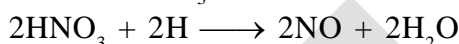
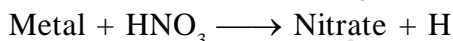
(ii) **Reaction with metal** concentrated nitric acid is a strong oxidising agent and attacks most metals except noble metals such as gold and platinum. Au & Pt dissolve in aqua regia a mixture of 25% conc.  $\text{HNO}_3$  & 75% conc. HCl. The products of oxidation depend upon the concentration of the acid, temperature and the nature of the material undergoing oxidation.

Ex.



Some metals (e.g., Cr, Al) do not dissolve in concentrated nitric acid because of the formation of a passive film of oxide on the surface.

Armstrong postulated that primary action of nitric acid is to produce hydrogen in the nascent form. Before this hydrogen is allowed to escape, it reduces the nitric acid into number of products like  $\text{NO}_2$ , NO,  $\text{N}_2\text{O}$ ,  $\text{N}_2$  or  $\text{NH}_3$  according to the following reactions:



The progress of the reaction is controlled by a number of factors :

- the nature of the metal,
- the concentration of the acid,
- the temperature of the reaction,
- the presence of other impurities.

| Concentration of nitric acid    | Metal          | Main Products                                                   |
|---------------------------------|----------------|-----------------------------------------------------------------|
| Very dilute $\text{HNO}_3$ (6%) | Mg, Mn         | $\text{H}_2$ + Metal nitrate                                    |
|                                 | Fe, Zn, Sn     | $\text{NH}_4\text{NO}_3$ + metal nitrate + $\text{H}_2\text{O}$ |
|                                 | Pb, Cu, Ag, Hg | NO + metal nitrate + $\text{H}_2\text{O}$                       |

Dilute  $\text{HNO}_3$  (20%)      Fe, Zn       $\text{N}_2\text{O} + \text{metal nitrate} + \text{H}_2\text{O}$

-----  
Sn       $\text{NH}_4\text{NO}_3 + \text{Sn}(\text{NO}_3)_2$

-----  
Zn, Fe, Pb, Cu, Ag       $\text{NO}_2 + \text{metal nitrate} + \text{H}_2\text{O}$

Conc.  $\text{HNO}_3$  (70%)      -----  
Sn       $\text{NO}_2 + \text{H}_2\text{SnO}_3$   
Metastannic acid

### Action on Proteins :

Nitric acid attacks proteins forming a yellow nitro compound called xanthoprotein. It, therefore, stains skin and renders wool yellow. This property is utilized for the test of proteins.

**Uses :** The major use of nitric acid is in the manufacture of ammonium nitrate for fertilisers and other nitrates for use in explosives and pyrotechnics. It is also used for the preparation of nitroglycerin, trinitrotoluene and other organic nitro compounds. Other major uses are in the **pickling of stainless steel**, etching of metals and as an oxidiser in rocket fuels.

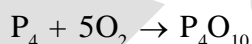
**Pickling** is a metal surface treatment used to remove impurities, such as stains, inorganic contaminants, rust or scale from ferrous metals, copper, precious metals and aluminium alloys. A solution called pickle liquor, which contains strong acids, is used to remove surface impurities.

### ALLOTROPIC FORMS OF PHOSPHORUS

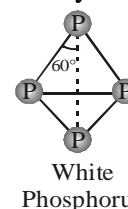
Phosphorus is found in many allotropic forms, the important ones being white, red and black. White phosphorus is a translucent white waxy solid. It is poisonous, insoluble in water but soluble in carbon disulphide and glows in dark (chemiluminescence). It dissolves in boiling NaOH solution in an inert atmosphere

giving  $\text{PH}_3$ .  $\text{P}_4 + 3\text{NaOH} + 3\text{H}_2\text{O} \longrightarrow \text{PH}_3 + 3\text{NaH}_2\text{PO}_2$   
(Sodium hypophosphite)

White phosphorus is less stable and therefore, more reactive than the other solid phases under normal conditions because of angular strain in the  $\text{P}_4$  molecule where the angles are only  $60^\circ$ . It readily catches fire in air to give dense white fumes of  $\text{P}_4\text{O}_{10}$ .

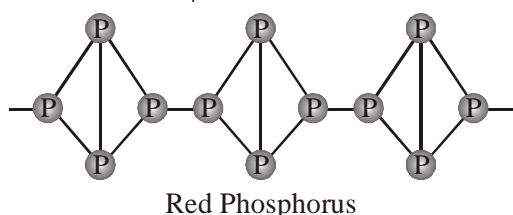


It consists of discrete tetrahedral  $\text{P}_4$  molecule as shown in Fig.



**Red phosphorus** is obtained by heating white phosphorus at 573K in an inert atmosphere for several days. When red phosphorus is heated under high pressure, a series of phases of black phosphorus is formed. Red phosphorus possesses iron grey lustre. It is odourless, nonpoisonous and insoluble in water as well as in carbon disulphide. Chemically, red phosphorus is much less reactive than white phosphorus. It does not glow in the dark.

It is polymeric, consisting of chains of  $\text{P}_4$  tetrahedra linked together in the manner as shown in Fig.



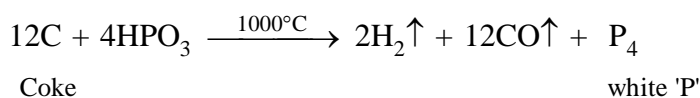
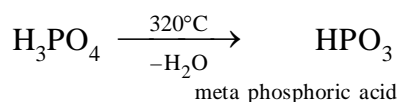
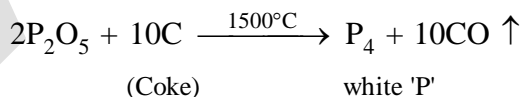
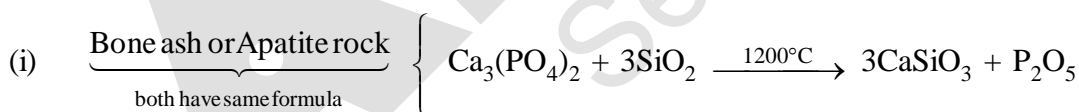
**Black phosphorus** has two forms  $\alpha$ -black phosphorus and  $\beta$ -black phosphorus.  $\alpha$ -Black phosphorus is formed when red phosphorus is heated in a sealed tube at 803K. It can be sublimed in air and has opaque monoclinic or rhombohedral crystals. It does not oxidise in air.  $\beta$ -Black phosphorus is prepared by heating white phosphorus at 473 K under high pressure. It does not burn in air upto 673 K.

**Note :** If white phosphorus is heated to about 250°C, or a lower temperature in the presence of sunlight, then red phosphorus is formed. Heating white phosphorus under high pressure results in a highly polymerized form of P called black phosphorus. This is thermodynamically the most stable allotrope.

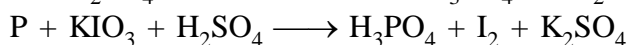
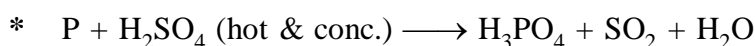
### Comparison between White and Red Phosphorus

| Property                      | White phosphorus                                       | Red phosphorus         |
|-------------------------------|--------------------------------------------------------|------------------------|
| Physical state                | Soft waxy solid.                                       | Brittle powder.        |
| Colour                        | White when pure.<br>Attains yellow colour on standing. | Red.                   |
| Odour                         | Garlic                                                 | Odourless.             |
| Solubility in water           | Insoluble.                                             | insoluble              |
| Solubility in CS <sub>2</sub> | Soluble.                                               | Insoluble.             |
| Physiological action          | Poisonous.                                             | Non-poisonous.         |
| Chemical activity             | Very active.                                           | Less active.           |
| Stability                     | Unstable.                                              | Stable.                |
| Phosphorescence               | Glow in dark                                           | Does not glow in dark. |
| Molecular formula             | P <sub>4</sub>                                         | Complex polymer.       |

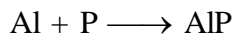
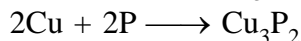
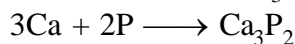
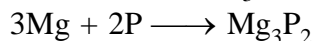
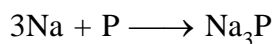
### Preparation of white 'P'



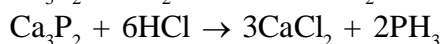
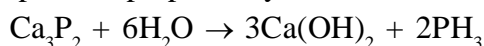


**Reactions of 'P'**

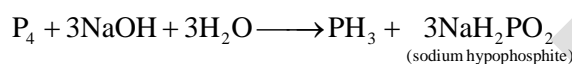
\* Reaction with hot metal —

**PHOSPHINE****Preparation**

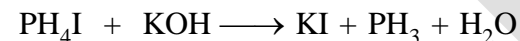
(i) Phosphine is prepared by the reaction of calcium phosphide with water or dilute HCl.



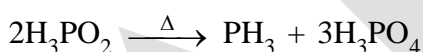
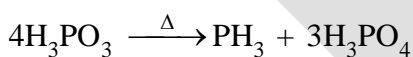
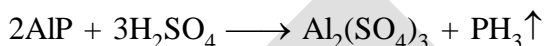
(ii) Laboratory preparation it is prepared by heating white phosphorus with concentrated NaOH solution in an inert atmosphere of  $\text{CO}_2$ .



Pure  $\text{PH}_3$  is non inflammable but becomes inflammable owing to the presence of  $\text{P}_2\text{H}_4$  or  $\text{P}_4$  vapours. To purify it from the impurities, it is absorbed in HI to form phosphonium iodide ( $\text{PH}_4\text{I}$ ) which on treating with KOH gives off phosphine.

**Other preparation**

( $\text{PH}_3 + \text{HI}$ )



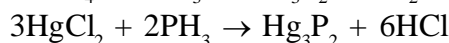
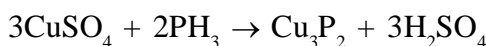
} Purest  $\text{PH}_3$

**Physical Properties :**

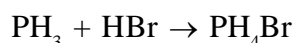
- It is a colourless gas with rotten fish smell and is highly poisonous.
- It explodes in contact with traces of oxidising agents like  $\text{HNO}_3$ ,  $\text{Cl}_2$  and  $\text{Br}_2$  vapours.
- It is slightly soluble in water but soluble in  $\text{CS}_2$ . The solution of  $\text{PH}_3$  in water decomposes in presence of light giving red phosphorus and  $\text{H}_2$ .

**Chemical Properties :**

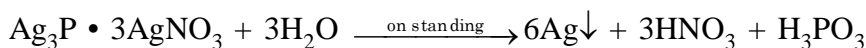
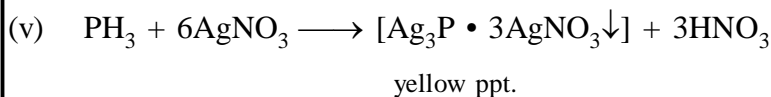
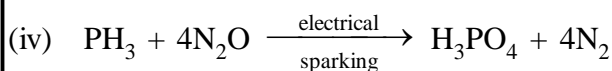
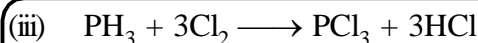
- It absorbed in copper sulphate or mercuric chloride solution, the corresponding phosphides are obtained.



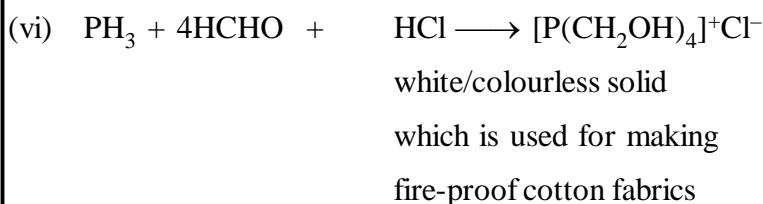
Phosphine is weakly basic and like ammonia, gives phosphonium compounds with acids e.g.,



- $\text{PH}_3 + \text{O}_2 \xrightarrow{150^\circ} \text{P}_2\text{O}_5 + \text{H}_2\text{O}$

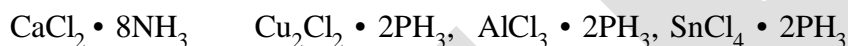
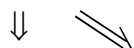


Black ppt.

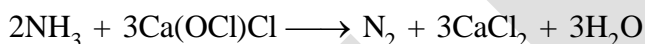
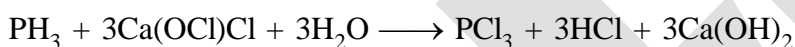


### Note :

Like  $\text{NH}_3$ ,  $\text{PH}_3$  also can form addition product.



$\text{PH}_3$  can be absorbed by  $\text{Ca}(\text{OCl})\text{Cl}$ .



### Uses :

(i) The spontaneous combustion of phosphine is technically used in Holme's signals. Containers containing calcium carbide and calcium phosphide are pierced and thrown in the sea when the gases evolved burn and serve as a signal.

(ii) It is also used in smoke screens.

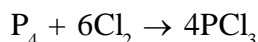
## PHOSPHORUS HALIDES

Phosphorus forms two types of halides,  $\text{PX}_3$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ) and  $\text{PX}_5$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}$ ).

### PHOSPHORUS TRICHLORIDE

#### Preparation

(i) By passing dry chlorine over heated white phosphorus.



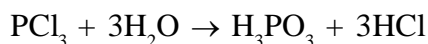
(ii) By the action of thionyl chloride with white phosphorus.



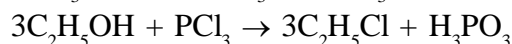
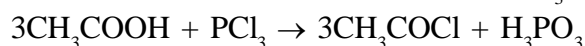
#### Properties

(i) It is a colourless oily liquid

(ii) Hydrolyses in the presence of moisture.



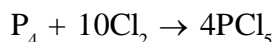
- (iii) It reacts with organic compounds containing –OH group such as  $\text{CH}_3\text{COOH}$ ,  $\text{C}_2\text{H}_5\text{OH}$ .



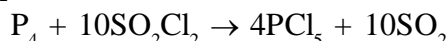
### PHOSPHORUS PENTACHLORIDE

#### Preparation

- (i) By the reaction of white phosphorus with excess of dry chlorine.

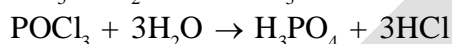
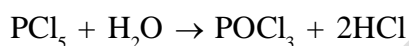


- (ii) By the action of  $\text{SO}_2\text{Cl}_2$  on phosphorus.

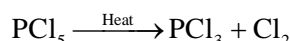


#### Properties :

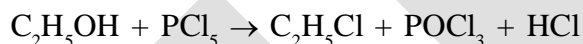
- (i)  $\text{PCl}_5$  is a yellowish white powder  
 (ii) It hydrolysis in moist air to  $\text{POCl}_3$  and finally gets converted to phosphoric acid.



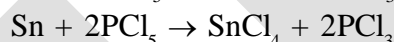
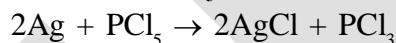
- (iii) When heated, it sublimes but decomposes on stronger heating.



- (iv) It reacts with organic compounds containing –OH group converting them to chloro derivatives.



- (v) Finely divided metals on heating with  $\text{PCl}_5$  give corresponding chlorides.

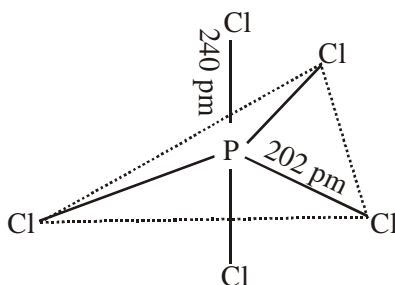


#### Uses :

It is used in the synthesis of some organic compounds, e.g.,  $\text{C}_2\text{H}_5\text{Cl}$ ,  $\text{CH}_3\text{COCl}$ .

#### Note :

In gaseous and liquid phases, it has a trigonal bipyramidal structure as shown. The three equatorial P–Cl bonds are equivalent, while the two axial bonds are longer than equatorial bonds. This is due to the fact that the axial bond pairs suffer more repulsion as compared to equatorial bond pairs.



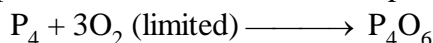
In the solid state it exists as an ionic solid,  $[\text{PCl}_4]^+[\text{PCl}_6]^-$  in which the cation,  $[\text{PCl}_4]^+$  is tetrahedral and the anion,  $[\text{PCl}_6]^-$  is octahedral.

**OXIDES OF PHOSPHORUS**

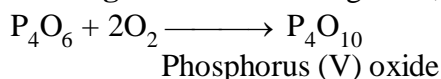
It forms three important oxides which exist in dimeric forms.

**PHOSPHORUS TRIOXIDE (P<sub>4</sub>O<sub>6</sub>)****Preparation**

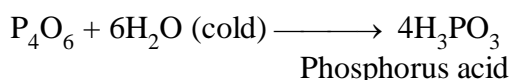
Phosphorus trioxides is formed when phosphorus is burnt in a limited supply of air and inert atmosphere.

**Properties**

- (a) **Heating in air :** On heating in air, it forms phosphorus pentoxide.



- (b) **Action of water :** It dissolves in cold water to give phosphorus acid.



It is, therefore, considered as anhydride of phosphorus acid.

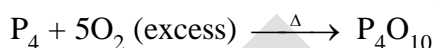
**Note:** With hot water, it gives phosphoric acid and inflammable phosphine.

**Structure**

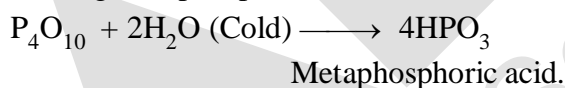
- (a) Each atom of phosphorus in P<sub>4</sub>O<sub>6</sub> is present at the corner of a tetrahedron  
 (b) Each phosphorus atom is covalently bonded to three oxygen atoms and each oxygen atom is bonded to two phosphorus atoms.  
 (c) It is clear from the structure that the six oxygen atoms lie along the edges of the tetrahedron of P atoms.

**PHOSPHORUS (V) OXIDE (P<sub>4</sub>O<sub>10</sub>)**

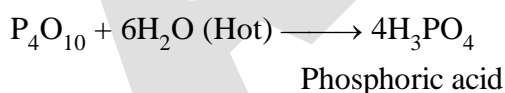
**Preparation :** It is prepared by heating white phosphorus in excess of air.

**Properties**

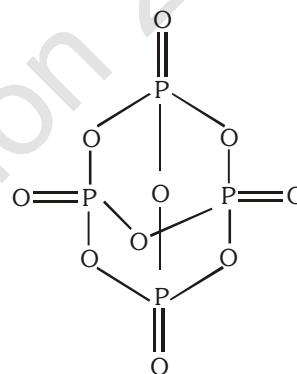
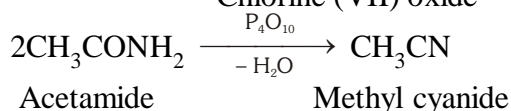
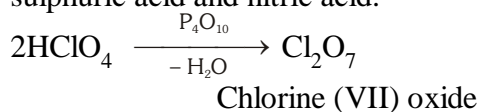
- (a) It is snowy white solid.  
 (b) **Action with water :** It readily dissolves in cold water forming metaphosphoric acid.



With hot water it gives phosphoric acid.



- (c) **Dehydrating nature :** Phosphorus pentoxide has strong affinity for water and, therefore, acts as a powerful dehydrating agent. It extracts water from many inorganic and organic compounds.  
 (d) P<sub>4</sub>O<sub>10</sub> is a very strong dehydrating agent and extracts water from many compounds including sulphuric acid and nitric acid.



### Structure

- Its structure is similar to that of  $P_4O_6$ .
- In addition, each phosphorus atom forms a double bond with oxygen atom as shown in figure.

### OXOACIDS OF PHOSPHORUS :

The important oxoacids of phosphorus with their formulae, methods of preparation and the presence of some characteristic bonds in their structures are given in a table.

Oxoacids of Phosphorus

| Name                          | Formula     | Oxidation state of Phosphorus | Characteristic bonds and their number          | Preparation                                       |
|-------------------------------|-------------|-------------------------------|------------------------------------------------|---------------------------------------------------|
| Hypophosphorus (Phosphinic)   | $H_3PO_2$   | + 1                           | One P — OH<br>Two P — H<br>One P = O           | white $P_4$ + alkali                              |
| Orthophosphorous (Phosphonic) | $H_3PO_3$   | + 3                           | Two P — OH<br>One P — H<br>One P = O           | $P_2O_3 + H_2O$                                   |
| Pyrophosphorous               | $H_4P_2O_5$ | + 3                           | Two P — OH<br>Two P — H<br>Two P = O           | $PCl_3 + H_3PO_3$                                 |
| Hypophosphoric                | $H_4P_2O_6$ | + 4                           | Four P — OH<br>Two P = O<br>One P — P          | red $P_4$ + alkali                                |
| Orthophosphoric               | $H_3PO_4$   | + 5                           | Three P — OH<br>One P = O                      | $P_4O_{10} + H_2O$                                |
| Pyrophosphoric                | $H_4P_2O_7$ | + 5                           | Four P — OH<br>Two P = O<br>One P — O — P      | heat phosphoric acid                              |
| Metaphosphoric*               | $(HPO_3)_n$ | + 5                           | Three P — OH<br>Three P = O<br>Three P — O — P | phosphorous acid + $Br_2$ , heat in a sealed tube |

### STRUCTURE OF OXOACID :

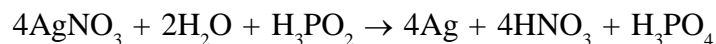
In oxoacids phosphorus is tetrahedrally surrounded by other atoms. All these acids contain at least one P=O bond and one P—OH bond. The oxoacids in which phosphorus has lower oxidation state (less than +5) contain, in addition to P=O and P—OH bonds, either P—P (e.g., in  $H_4P_2O_6$ ) or P—H (e.g., in  $H_3PO_2$ ) bonds but not both.  $H_3PO_3$  and  $H_3PO_2$  are diacidic and monobasic respectively.

Note :-

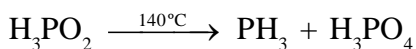
- These acids in +3 oxidation state of phosphorus tend to disproportionate to higher and lower oxidation states. For example, phosphorous acid on heating disproportionates to give orthophosphoric acid (or phosphoric acid) and phosphine.



- (ii) The acids which contain P–H bond have strong reducing properties. Thus, hypophosphorous acid is a good reducing agent as it contains two P–H bonds and reduces,  $\text{AgNO}_3$  to metallic silver.

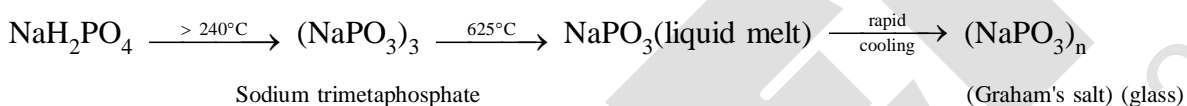


### Heating Effect :



### Graham salt

Graham's salt is the best known of these long chain polyphosphates, and is formed by quenching molten  $\text{NaPO}_3$ . Graham's salt is soluble in water. These solutions give precipitates with metal ions such as  $\text{Pb}^{2+}$  and  $\text{Ag}^+$  but not with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . Graham's salt is sold commercially under the trade name Calgon. In industry it is incorrectly called sodium hexametaphosphate crystallizing. It is widely used for softening water.



## OXYGEN FAMILY

## GROUP 16 ELEMENTS (O, S, Se, Te, Po)

This is sometimes known as group of chalcogens.

### ❑ Occurrence

Oxygen is the most abundant of all the elements on earth crust. Oxygen forms about 46.6% by mass of earth's crust. Dry air contains 20.946% oxygen by volume. However, the abundance of sulphur in the earth's crust is only 0.03-0.1%. Combined sulphur exists primarily as sulphates such as gypsum  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , epsom salt  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , baryte  $\text{BaSO}_4$  and sulphides such as galena  $\text{PbS}$ , zinc blende  $\text{ZnS}$ , copper pyrites  $\text{CuFeS}_2$ . Traces of sulphur occur as hydrogen sulphide in volcanoes. Organic materials such as eggs, proteins, garlic, onion, mustard, hair and wool contain sulphur.

Selenium and tellurium are also found as metal selenides and tellurides in sulphide ores. Polonium occurs in nature as a decay product of thorium and uranium minerals.

### ❑ Electronic Configuration

$ns^2np^4$  is the general valence shell electronic configuration.

### ❑ Atomic and Ionic Radii : Covalent radius : $\text{O} < \text{S} < \text{Se} < \text{Te}$

### ❑ Ionisation Enthalpy : $\text{O} > \text{S} > \text{Se} > \text{Te} > \text{Po}$ ( $\text{IE}_1$ values)

### ❑ Most Negative Electron Gain Enthalpy: $\text{S} > \text{Se} > \text{Te} > \text{Po} > \text{O}$

### ❑ Electronegativity : $\text{O} > \text{S} > \text{Se} > \text{Te}$

### ❑ Metallic Character : $\text{O} < \text{S} < \text{Se} < \text{Te} < \text{Po}$

### ❑ Melting and Boiling points :

M.P. :  $\text{Te} > \text{Po} > \text{Se} > \text{S} > \text{O}$

B.P. :  $\text{Te} > \text{Po} > \text{Se} > \text{S} > \text{O}$

### Elemental State

Oxygen exist as diatomic molecular gas in this case there is  $p\pi - p\pi$  overlap thus two O atoms form double bond  $\text{O} = \text{O}$ . The intermolecular forces in  $\text{O}_2$  are weak VB forces.  $\therefore \text{O}_2$  exist as gas. On the other hand, other elements of family do not form stable  $p\pi - p\pi$  bonds and do not exist as  $\text{M}_2$  molecules. Other atoms are linked by single bonds and form poly atomic complex molecules for eg.  $\text{S} - \text{S}_8$ ,  $\text{Se} - \text{Se}_8$

### Allotropy

All element exhibit allotropy for e.g.

**Oxygen** –  $\text{O}_2$  and  $\text{O}_3$

Liquid  $\text{O}_2$  - pale blue

Solid  $\text{O}_2$  - blue





### ❑ Anomalous behaviour of oxygen

The anomalous behaviour of oxygen, like other members of p-block present in second period is due to its small size and high electronegativity. One typical example of effects of small size and high electronegativity is the presence of strong hydrogen bonding in  $\text{H}_2\text{O}$  which is not found in  $\text{H}_2\text{S}$ . The absence of d orbitals in oxygen limits its covalency to four and in practice, rarely exceeds two. On the other hand, in case of other elements of the group, the valence shells can be expanded and covalency exceeds four.

### (I) Reactivity with hydrogen:

- All the elements of Group 16 form hydrides of the type  $\text{H}_2\text{E}$  ( $\text{E} = \text{O}, \text{S}, \text{Se}, \text{Te}, \text{Po}$ ).
- Their acidic character increases from  $\text{H}_2\text{O}$  to  $\text{H}_2\text{Te}$ . The increase in acidic character can be explained in terms of decrease in bond enthalpy for the dissociation of  $\text{H}-\text{E}$  bond down the group. Owing to the decrease in enthalpy for the dissociation of  $\text{H}-\text{E}$  bond down the group, the thermal stability of hydrides also decreases from  $\text{H}_2\text{O}$  to  $\text{H}_2\text{Po}$ .
- All the hydrides except water possess reducing property and this character increases from  $\text{H}_2\text{S}$  to  $\text{H}_2\text{Te}$ .

Properties of Hydrides of Group 16 Elements

| Property                                                          | $\text{H}_2\text{O}$  | $\text{H}_2\text{S}$ | $\text{H}_2\text{Se}$ | $\text{H}_2\text{Te}$ |
|-------------------------------------------------------------------|-----------------------|----------------------|-----------------------|-----------------------|
| m.p./K                                                            | 273                   | 188                  | 208                   | 222                   |
| b.p./K                                                            | 373                   | 213                  | 232                   | 269                   |
| $\text{H}-\text{E}$ distance /pm                                  | 96                    | 134                  | 146                   | 169                   |
| $\text{HEH}$ angle ( $^\circ$ )                                   | 104                   | 92                   | 91                    | 90                    |
| $\Delta_f H / \text{kJ mol}^{-1}$                                 | -286                  | -20                  | 73                    | 100                   |
| $\Delta_{\text{diss}} H (\text{H}-\text{E}) / \text{kJ mol}^{-1}$ | 463                   | 347                  | 276                   | 238                   |
| Dissociation constant <sup>a</sup>                                | $1.8 \times 10^{-16}$ | $1.3 \times 10^{-7}$ | $1.3 \times 10^{-4}$  | $2.3 \times 10^{-3}$  |

### (II) Reactivity with oxygen:

- All these elements form oxides of the  $\text{EO}_2$  and  $\text{EO}_3$  types where  $\text{E} = \text{S}, \text{Se}, \text{Te}$  or  $\text{Po}$ .
- Ozone ( $\text{O}_3$ ) and sulphur dioxide ( $\text{SO}_2$ ) are gases while selenium dioxide ( $\text{SeO}_2$ ) is solid.
- Reducing property of dioxide decreases from  $\text{SO}_2$  to  $\text{TeO}_2$ ;  $\text{SO}_2$  is reducing while  $\text{TeO}_2$  is an oxidising agent.
- Besides  $\text{EO}_2$  type, sulphur, selenium and tellurium also form  $\text{EO}_3$  type oxides ( $\text{SO}_3, \text{SeO}_3, \text{TeO}_3$ ). Both types of oxides are acidic in nature.

### (III) Reactivity towards the halogens:

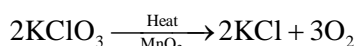
- Elements of Group 16 form a large number of halides of the type,  $\text{EX}_6, \text{EX}_4$  and  $\text{EX}_2$  where  $\text{E}$  is an element of the group and  $\text{X}$  is a halogen.
- The stability of the halides decreases in the order  $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$ .
- Amongst hexahalides, hexafluorides are the only stable halides. All hexafluorides are gaseous in nature. They have octahedral structure. Sulphur hexafluoride,  $\text{SF}_6$  is exceptionally stable for steric reasons.

Amongst tetrafluorides,  $\text{SF}_4$  is a gas,  $\text{SeF}_4$  a liquid and  $\text{TeF}_4$  a solid. These fluorides have  $sp^3d$  hybridisation and thus, have trigonal bipyramidal structures in which one of the equatorial positions is occupied by a lone pair of electrons. This geometry is also regarded as see-saw geometry. All elements except oxygen form dichlorides and dibromides (because they form oxides). These dihalides are formed by  $sp^3$  hybridisation and thus, have tetrahedral structure. The well known monohalides are dimeric in nature. Examples are  $\text{S}_2\text{F}_2$ ,  $\text{S}_2\text{Cl}_2$ ,  $\text{S}_2\text{Br}_2$ ,  $\text{Se}_2\text{Cl}_2$  and  $\text{Se}_2\text{Br}_2$ . These dimeric halides undergo disproportionation as given below :  $2\text{Se}_2\text{Cl}_2 \rightarrow \text{SeCl}_4 + 3\text{Se}$

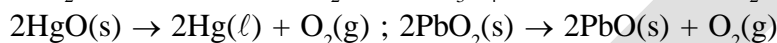
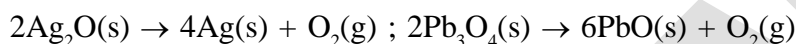
### DIOXYGEN

#### (a) Laboratory method

(i) By heating oxygen containing salts such as chlorates, nitrates and permanganates.



(ii) By the thermal decomposition of the oxides of metals low in the electrochemical series and higher oxides of some metals.



(iii) Hydrogen peroxide is readily decomposed into water and dioxygen by catalysts such as finely divided metals and manganese dioxide.

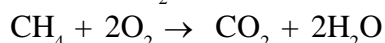
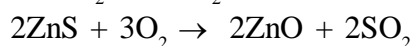
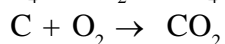
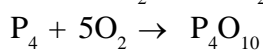
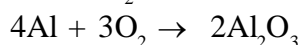
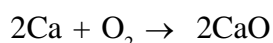


(b) **Large scale preparation** : It can be prepared from water or air. Electrolysis of water leads to the release of hydrogen at the cathode and oxygen at the anode.

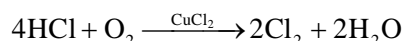
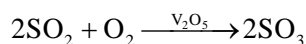
(c) **Industrially method** : Dioxygen is obtained from air by first removing carbon dioxide and water vapour and then, the remaining gases are liquefied and fractionally distilled to give dinitrogen and dioxygen.

#### Properties

- Dioxygen is a colourless and odourless gas.
- Its solubility in water is to the extent of  $3.08 \text{ cm}^3$  in  $100 \text{ cm}^3$  water at  $293 \text{ K}$  which is just sufficient for the vital support of marine and aquatic life.
- It liquefies at  $90 \text{ K}$  and freezes at  $55 \text{ K}$ .
- Oxygen atom has three stable isotopes:  $^{16}\text{O}$ ,  $^{17}\text{O}$  and  $^{18}\text{O}$ . Molecular oxygen,  $\text{O}_2$  is unique in being paramagnetic inspite of having even number of electrons.
- Dioxygen directly reacts with nearly all metals and non-metals except some metals (e.g., Au, Pt) and some noble gases. Its combination with other elements is often strongly exothermic which helps in sustaining the reaction. However, to initiate the reaction, some external heating is required as bond dissociation enthalpy of oxygen-oxygen double bond is high ( $493.4 \text{ kJ mol}^{-1}$ ). Some of the reactions of dioxygen with metals, non-metals and other compounds are as follows :



Some compounds are catalytically oxidised. For example,



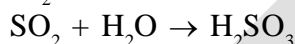
- Uses:** (i) It's importance in normal respiration and combustion processes, oxygen is used in oxyacetylene welding, in the manufacture of many metals, particularly steel.  
 (ii) Oxygen cylinders are widely used in hospitals, high altitude flying and in mountaineering.  
 (iii) The combustion of fuels, e.g., hydrazines in liquid oxygen, provides tremendous thrust in rockets.

### SIMPLE OXIDES

A binary compound of oxygen with another element is called oxide. In many cases one element forms two or more oxides. The oxides vary widely in their nature and properties. Oxides can be simple (e.g.,  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ ) or mixed ( $\text{Pb}_3\text{O}_4$ ,  $\text{Fe}_3\text{O}_4$ ).

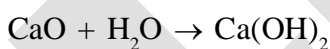
**Types of simple oxide :** Simple oxides can be classified on the basis of their acidic, basic or amphoteric character.

**Acidic oxide :** An oxide that combines with water to give an acid is termed acidic oxide (e.g.,  $\text{SO}_2$ ,  $\text{Cl}_2\text{O}_7$ ,  $\text{CO}_2$ ,  $\text{N}_2\text{O}_5$ ). For example,  $\text{SO}_2$  combines with water to give  $\text{H}_2\text{SO}_3$ , an acid.



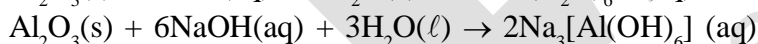
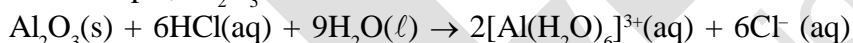
As a general rule, only non-metal oxides are acidic but oxides of some metals in high oxidation state also have acidic character (e.g.,  $\text{Mn}_2\text{O}_7$ ,  $\text{CrO}_3$ ,  $\text{V}_2\text{O}_5$ ).

**Basic oxide :** The oxides which give a base with water are known as basic oxides (e.g.,  $\text{Na}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{BaO}$ ). In general, metallic oxides are basic. For example,  $\text{CaO}$  combines with water to give  $\text{Ca(OH)}_2$ , a base.



### Amphoteric oxide :

Some metallic oxides exhibit a dual behaviour. They show characteristics of both acidic as well as basic oxides. Such oxides are known as amphoteric oxides. They react with acids as well as alkalies. For example,  $\text{Al}_2\text{O}_3$  reacts with acids as well as alkalies.



### Neutral oxide:

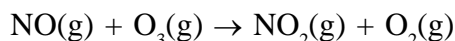
There are some oxides which are neither acidic nor basic. Such oxides are known as neutral oxides. Examples of neutral oxides are  $\text{CO}$ ,  $\text{NO}$  and  $\text{N}_2\text{O}$ .

### OZONE

- (i) Ozone is an allotropic form of oxygen and is diamagnetic.  
 (ii) It is too reactive to remain for long in the atmosphere at sea level. At a height of about 20 kilometres, it is formed from atmospheric oxygen in the presence of sunlight. This ozone layer protects the earth's surface from an excessive concentration of ultraviolet (UV) radiations.

### Threats to ozone layer

- (i) Experiments have shown that nitrogen oxides (particularly nitric oxide) combine very rapidly with ozone and there is, thus, the possibility that nitrogen oxides emitted from the exhaust systems of supersonic jet aeroplanes might be slowly depleting the concentration of the ozone layer in the upper atmosphere.



- (ii) Another threat to this ozone layer is probably posed by the use of freons which are used in aerosol sprays and as refrigerants.

**Preparation**

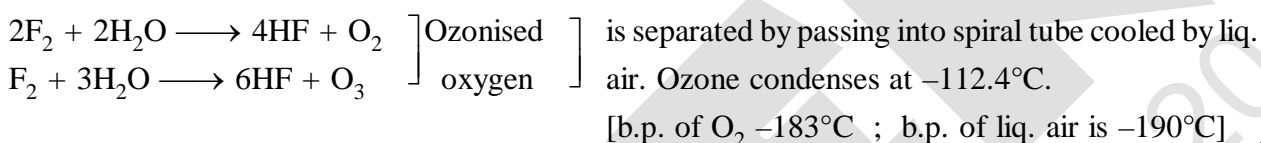
When a slow dry stream of oxygen is passed through a silent electrical discharge, conversion of oxygen to ozone (10%) occurs. The product is known as ozonised oxygen.



Since the formation of ozone from oxygen is an **endothermic** process, it is necessary to use a silent electrical discharge in its preparation to prevent its decomposition. If concentration of ozone greater than 10 percent is required, a battery of ozonisers can be used, and pure ozone (b.p.  $-112.4^\circ\text{C}$ ) can be condensed in a vessel surrounded by liquid oxygen.

**Ques.** Ozone is thermodynamically unstable with respect to oxygen. Explain ?

**Sol.** Because its decomposition into oxygen results in the liberation of heat ( $\Delta H$  is negative) and an increase in entropy ( $\Delta S$  is positive). These two effects reinforce each other, resulting in large negative Gibbs energy change ( $\Delta G$ ) for its conversion into oxygen.

**Note :****Properties**

- Pure ozone is a pale blue gas, dark blue liquid and violet-black solid.
- Ozone has a characteristic fishy smell and in small concentrations it is harmless.

**Toxic effect :**

- Toxic enough (more toxic than KCN). Its intense blue colour is due to the absorption of red light.
- However, if the concentration rises above about 100 parts per million, breathing becomes uncomfortable resulting in headache and nausea.

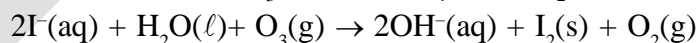
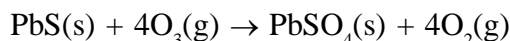
**Oxidizing properties**

It is one of best oxidising agent, in acid solution, its standard, reduction potential value is 2.07 V.

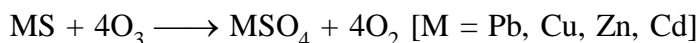


It is next to  $\text{F}_2$ . [above 2.07 V, only  $\text{F}_2$ ,  $\text{F}_2\text{O}$  are there]

It is not really surprising, therefore, high concentrations of ozone can be dangerously explosive. Due to the ease with which it liberates atoms of nascent oxygen ( $\text{O}_3 \rightarrow \text{O}_2 + \text{O}$ ), it acts as a powerful oxidising agent. For example, it oxidises lead sulphide to lead sulphate and iodide ions to iodine.

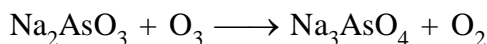
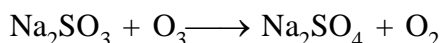


- Metal Sulphides to Sulphates.

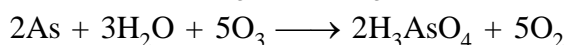
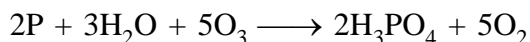
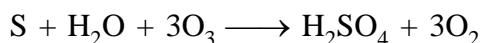


- $2\text{HX} + \text{O}_3 \longrightarrow \text{X}_2 + \text{H}_2\text{O} + \text{O}_2 \quad [\text{X} = \text{Cl, Br, I}]$

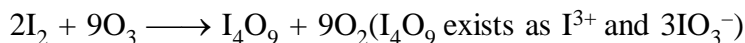
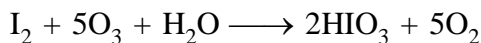
- $\text{NaNO}_2 + \text{O}_3 \longrightarrow \text{NaNO}_3 + \text{O}_2$



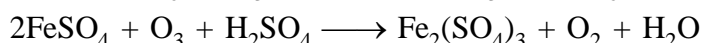
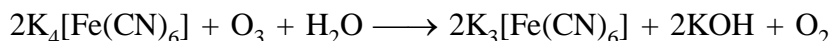
(iv) Moist S, P, As + O<sub>3</sub> ⇒



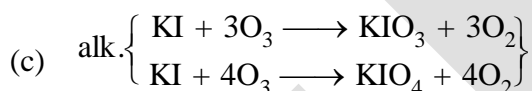
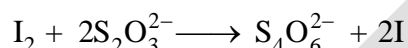
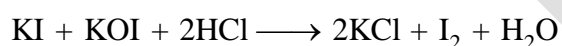
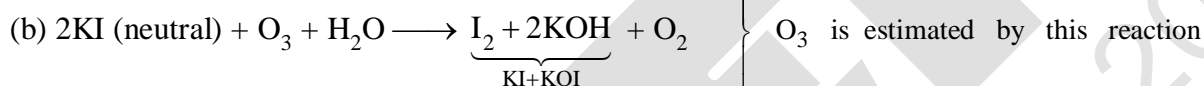
(v) Moist I<sub>2</sub> → HIO<sub>3</sub> whereas dry iodine → I<sub>4</sub>O<sub>9</sub> (yellow)



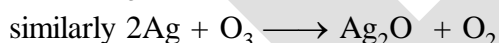
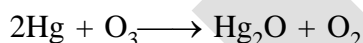
(vi) 2K<sub>2</sub>MnO<sub>4</sub> + O<sub>3</sub> + H<sub>2</sub>O → 2KMnO<sub>4</sub> + 2KOH + O<sub>2</sub>



(vii)(a) 2KI (acidified) + O<sub>3</sub> + 2HCl → I<sub>2</sub> + 2KCl + H<sub>2</sub>O + O<sub>2</sub>

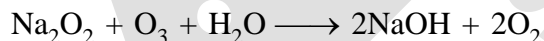
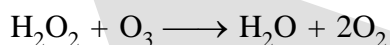


(viii) Hg loses its fluidity (tailing of Hg)



Brown

(ix) BaO<sub>2</sub> + O<sub>3</sub> → BaO + 2O<sub>2</sub>



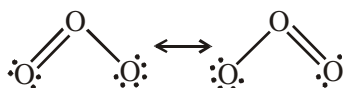
(x) 2KOH + 5O<sub>3</sub> → 2KO<sub>3</sub> + 5O<sub>2</sub> + H<sub>2</sub>O

**In all above reaction O<sub>3</sub> gives up O<sub>2</sub> but some reactions are there which consumes all O-atom.**

(i) 3SO<sub>2</sub> + O<sub>3</sub> → 3SO<sub>3</sub>

(ii) 3SnCl<sub>2</sub> + 6HCl + O<sub>3</sub> → 3SnCl<sub>4</sub> + 3H<sub>2</sub>O

**Bonding in ozone :** In ozone the two oxygen-oxygen bond lengths in the ozone molecule are identical (128 pm) and the molecule is angular as expected with a bond angle of about 117°. It is a resonance hybrid of two main forms given below:



**Absorbent :** (i) Turpentine oil (ii) Oil of cinnamon

**Quantitative method for the estimating on Ozone :** Ozone reacts with an excess of potassium iodide solution buffered with a borate buffer (pH 9.2), iodine is liberated which can be titrated against a standard solution of sodium thiosulphate.

**Uses :** (i) Sterilising water

(ii) Detection of position of the double bond in the unsaturated compound.

(iii) It is used as a germicide, disinfectant and for sterilising water.

(iv) It is also used for bleaching oils, ivory, flour, starch, etc.

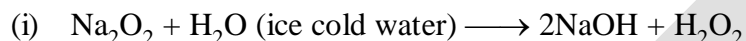
(v) It acts as an oxidising agent in the manufacture of potassium permanganate.

## ❑ HYDROGEN PEROXIDE ( $\text{H}_2\text{O}_2$ )

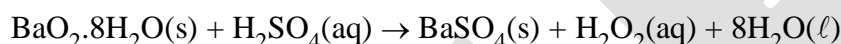
Hydrogen peroxide is an important chemical used in pollution control treatment of domestic and industrial effluents.

### Preparation

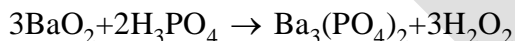
It can be prepared by the following methods.



(ii) Acidifying barium peroxide and removing excess water by evaporation under reduced pressure gives hydrogen peroxide.

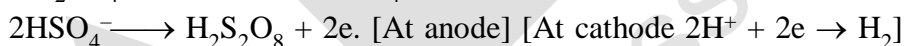
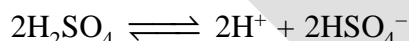


Instead of  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$  is added now-a-days because  $\text{H}_2\text{SO}_4$  catalyses the decomposition of  $\text{H}_2\text{O}_2$  whereas  $\text{H}_3\text{PO}_4$  favours to restore it.

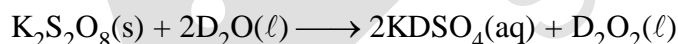


and,  $\text{Ba}_3(\text{PO}_4)_2 + 3\text{H}_2\text{SO}_4 \rightarrow 3\text{BaSO}_4 + 2\text{H}_3\text{PO}_4$  (reused again)

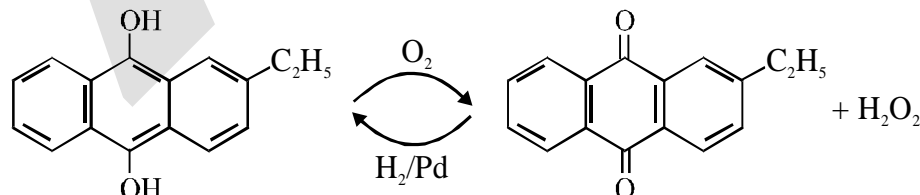
(iii) Peroxodisulphate, obtained by electrolytic oxidation of acidified sulphate solutions at high current density, on hydrolysis yields hydrogen peroxide.



This method is now used for the laboratory preparation of  $\text{D}_2\text{O}_2$ .



(iii) Industrially it is prepared by the autooxidation of 2-alkylanthraquinols.



2-ethylanthraquinol

2-ethylanthraquinone

In this case 1%  $\text{H}_2\text{O}_2$  is formed. It is extracted with water and concentrated to ~30% (by mass) by distillation under reduced pressure. It can be further concentrated to ~85% by careful distillation under low pressure. The remaining water can be frozen out to obtain pure  $\text{H}_2\text{O}_2$ .

### Physical Properties

In the pure state  $\text{H}_2\text{O}_2$  is an almost colourless (very pale blue) liquid. Its important physical properties are given in Table.  $\text{H}_2\text{O}_2$  is miscible with water in all proportions and forms a hydrate  $\text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$  (mp 221K). A 30% solution of  $\text{H}_2\text{O}_2$  is marketed as '100 volume' hydrogen peroxide. It means that one millilitre of 30%  $\text{H}_2\text{O}_2$  solution will give 100 mL of oxygen at STP. Commercially marketed sample is 10 V, which means that the sample contains 3%  $\text{H}_2\text{O}_2$ .

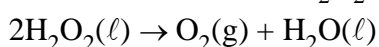
30% (w / v) or "100 V"  $\text{H}_2\text{O}_2$  solution is called **per hydrol**.

### Problem

Calculate the strength of 10 volume solution of hydrogen peroxide.

### Solution

10 volume solution of  $\text{H}_2\text{O}_2$  means that 1L of this  $\text{H}_2\text{O}_2$  solution will give 10 L of oxygen at STP



On the basis of above equation 22.7 L of  $\text{O}_2$  is produced from 68 g  $\text{H}_2\text{O}_2$  at STP 10 L of  $\text{O}_2$  at STP is produced from

$$\frac{68 \times 10}{22.7} \text{ g} = 29.9 \text{ g} \quad 30 \text{ g } \text{H}_2\text{O}_2$$

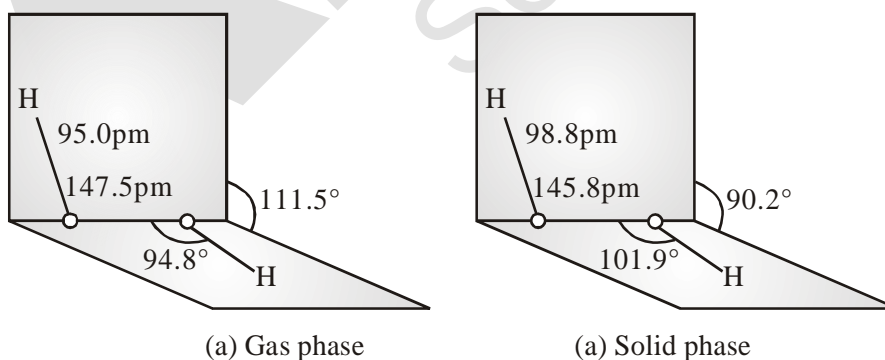
Therefore, strength of  $\text{H}_2\text{O}_2$  in 10 volume  $\text{H}_2\text{O}_2$  solution = 30 g/L = 3%  $\text{H}_2\text{O}_2$  solution

### Physical Properties of Hydrogen Peroxide

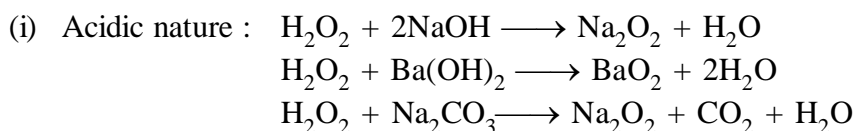
|                                              |       |                                                                 |                        |
|----------------------------------------------|-------|-----------------------------------------------------------------|------------------------|
| Melting point/K                              | 272.4 | Density (liquid at 298K)/g cm <sup>-3</sup>                     | 1.44                   |
| Boiling point (extrapolated)/K               | 423   | Viscosity (290 K)/centipoise                                    | 1.25                   |
| Vapour pressure (298K) mmHg                  | 1.9   | Dielectric constant (298K)/C <sup>2</sup> /N m <sup>2</sup>     | 70.7                   |
| Density (solid at 268.5K)/g cm <sup>-3</sup> | 1.64  | Electrical conductivity (298K)/Ω <sup>-1</sup> cm <sup>-1</sup> | 5.1 × 10 <sup>-8</sup> |

### Structure

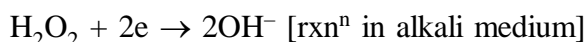
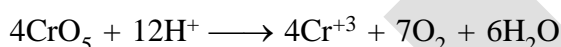
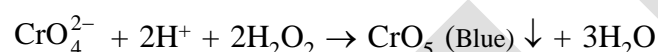
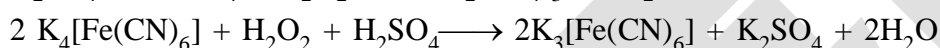
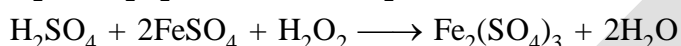
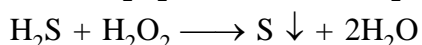
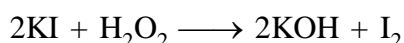
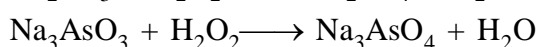
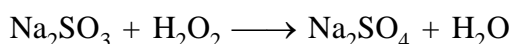
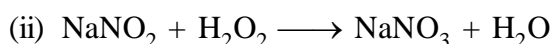
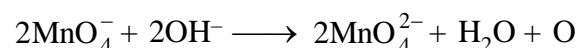
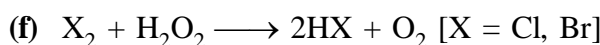
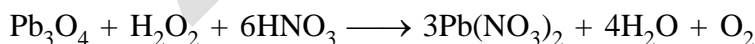
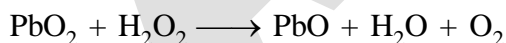
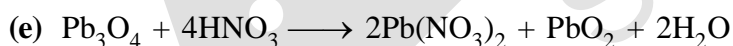
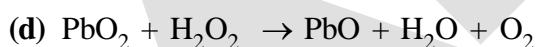
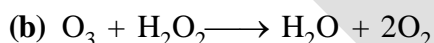
Hydrogen peroxide has a non-planar structure. The molecular dimensions in the gas phase and solid phase are shown in Fig.



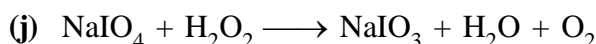
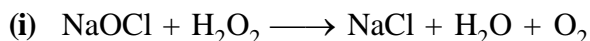
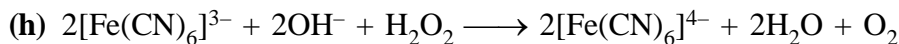
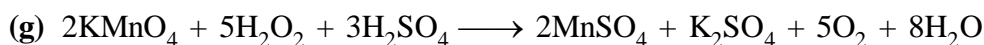
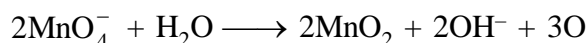
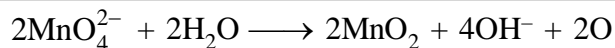
**Fig.** (a)  $\text{H}_2\text{O}_2$  structure in gas phase, dihedral angle is 111.5°. (b)  $\text{H}_2\text{O}_2$  structure in solid phase at 110K, dihedral angle is 90.2°.

**Chemical Properties:**

(ii) It is oxidant as well as reductant.

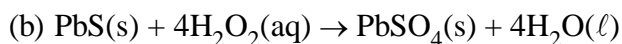
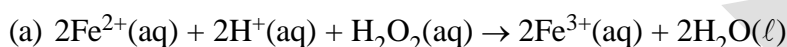
**Oxidising Properties:****Reducing properties:**



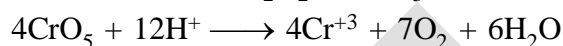
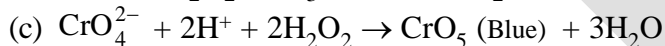
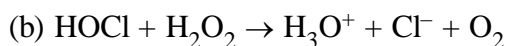
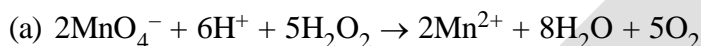


It acts as an oxidising as well as reducing agent in both acidic and alkaline media. Simple reactions are described below.

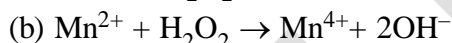
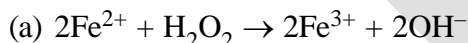
(i) Oxidising action in acidic medium



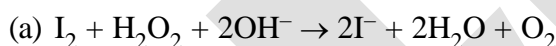
(ii) Reducing action in acidic medium



(iii) Oxidising action in basic medium



(iv) Reducing action in basic medium



#### ♦ Storage

$\text{H}_2\text{O}_2$  decomposes slowly on exposure to light.



In the presence of metal surfaces or traces of alkali (present in glass containers), the above reaction is catalysed. It is, therefore, stored in wax-lined glass or plastic vessels in dark. Acetanalide or Glycerol or Urea can be added as a stabiliser. It is kept away from dust because dust can induce explosive decomposition of the compound.

#### Uses

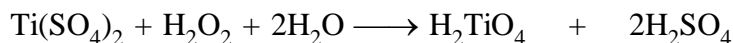
Its wide scale use has led to tremendous increase in the industrial production of  $\text{H}_2\text{O}_2$ .

Some of the uses are listed below :

- (i) In daily life it is used as a hair bleach and as a mild disinfectant. As an antiseptic it is sold in the market as perhydrol.

- (ii) It is used to manufacture chemicals like sodium perborate and per-carbonate, which are used in high quality detergents.
- (iii) It is used in the synthesis of hydroquinone, tartaric acid and certain food products and pharmaceuticals (cephalosporin) etc.
- (iv) It is employed in the industries as a bleaching agent for textiles, paper pulp, leather, oils, fats, etc.
- (v) As a rocket propellant:  

$$\text{NH}_2\text{NH}_2 + 2\text{H}_2\text{O}_2 \longrightarrow \text{N}_2 + 4\text{H}_2\text{O}$$
 [highly exothermic and large increase in volume]
- (vi) In detection of  $\text{Cr}^{+3}$ ,  $\text{Ti}^{+4}$  etc.



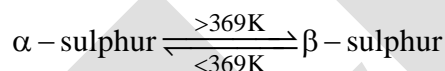
Yellow or orange

Pertitanic acid

- (vii) Nowadays it is also used in Environmental (Green) Chemistry. For example, in pollution control treatment of domestic and industrial effluents, oxidation of cyanides, restoration of aerobic conditions to sewage wastes, etc.

### ALLOTROPIC FORMS OF SULPHUR

Sulphur forms numerous allotropes of which the yellow rhombic ( $\alpha$ -sulphur) and monoclinic ( $\beta$ -sulphur) forms are the most important. The stable form at room temperature is rhombic sulphur, which transforms to monoclinic sulphur when heated above 369 K.



At 369 K both the forms are stable. This temperature is called transition temperature.

#### ❑ Rhombic sulphur ( $\alpha$ -sulphur)

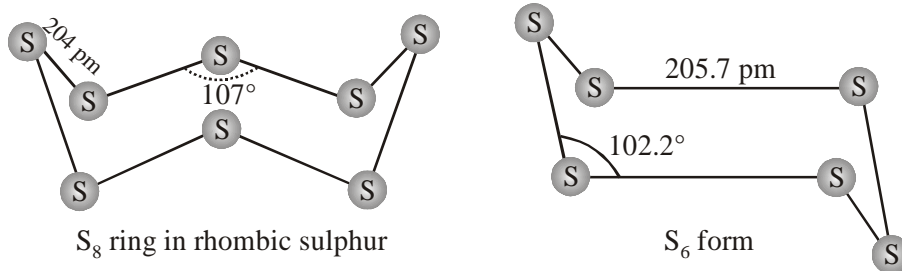
- (i) This allotrope is yellow in colour, m.p. 385.8 K and specific gravity 2.06.
- (ii) Rhombic sulphur crystals are formed on evaporating the solution of roll sulphur in  $\text{CS}_2$ .
- (iii) It is insoluble in water but dissolves to some extent in benzene, alcohol and ether.
- (iv) It is readily soluble in  $\text{CS}_2$ .

#### ❑ Monoclinic sulphur ( $\beta$ -sulphur)

- (i) Its m.p. is 393 K and specific gravity 1.98.
- (ii) It is soluble in  $\text{CS}_2$ .
- (iii) This form of sulphur is prepared by melting rhombic sulphur in a dish and cooling, till crust is formed. Two holes are made in the crust and the remaining liquid poured out. On removing the crust, colourless needle shaped crystals of  $\beta$ -sulphur are formed. It is stable above 369 K and transforms into  $\alpha$ -sulphur below it. Conversely,  $\alpha$ -sulphur is stable below 369 K and transforms into  $\beta$ -sulphur above this.

#### Structure of $\alpha$ and $\beta$ sulphur

Both rhombic and monoclinic sulphur have  $\text{S}_8$  molecules. These  $\text{S}_8$  molecules are packed to give different crystal structures. The  $\text{S}_8$  ring in both the forms is puckered and has a crown shape.



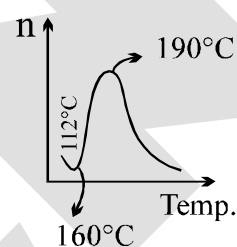
Several other modifications of sulphur containing 6-20 sulphur atoms per ring have been synthesised in the last two decades. In cyclo-S<sub>6</sub>, the ring adopts the chair form. At elevated temperatures (~1000 K), S<sub>2</sub> is the dominant species and is paramagnetic like O<sub>2</sub>.

**Note: Viscosity of 'S' with temperature :**

m.p. of 'S'  $\longrightarrow$  112.8°C.

> 112.8°C to 160°C  $\Rightarrow$  slow decreases due to S<sub>8</sub> rings slip and roll over one another easily.

> 160°C, increases sharply due to breaking of S<sub>8</sub> rings into chains and polymers into large size chain.



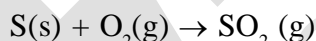
**Amorphous forms are**

- (i) Plastic sulphur      (ii) Milk of sulphur      (iii) Colloidal sulphur

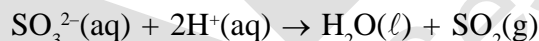
**SULPHUR DIOXIDE**

**Preparation**

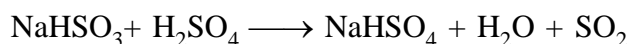
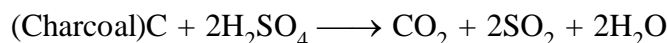
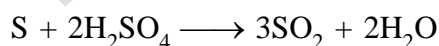
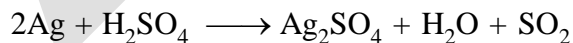
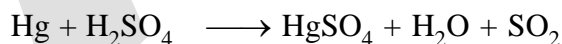
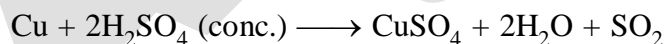
Sulphur dioxide is formed together with a little (6-8%) sulphur trioxide when sulphur is burnt in air or oxygen:



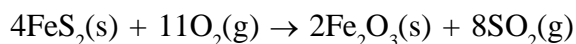
**laboratory method** by treating a sulphite with dilute sulphuric acid.



**other preparation :**



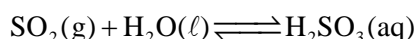
**Industrial method**, by-product of the roasting of sulphide ores.



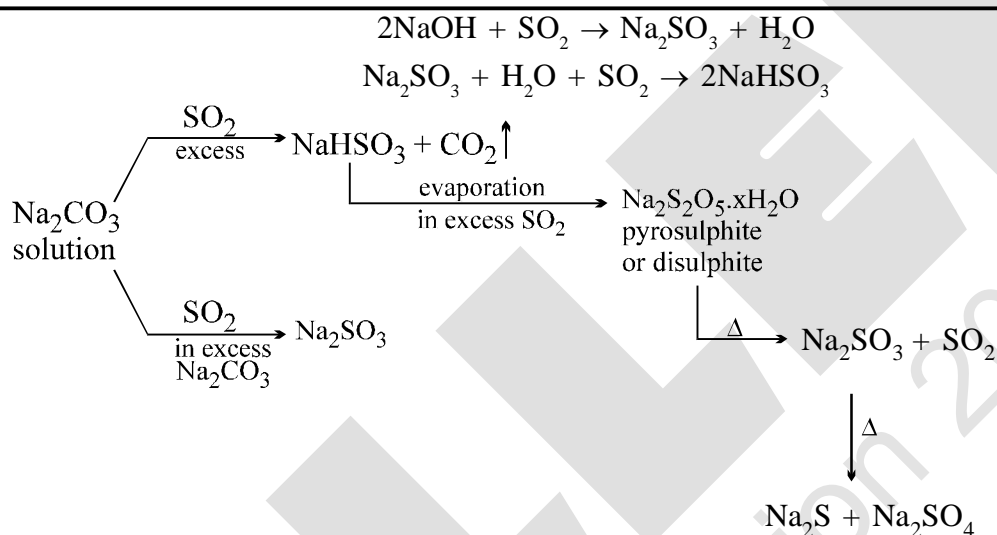
The gas after drying is liquefied under pressure and stored in steel cylinders.

### Properties

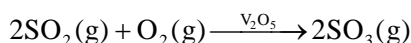
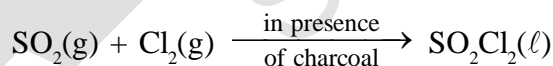
- (i) Sulphur dioxide is a colourless gas with pungent smell.
- (ii) It is highly soluble in water.
- (iii) It liquefies at room temperature under a pressure of two atmospheres and boils at 263 K.
- (iv) **Acidic character:** sulphur dioxide, when passed through water, forms a solution of sulphurous acid.



It reacts readily with sodium hydroxide solution, forming sodium sulphite, which then reacts with more sulphur dioxide to form sodium hydrogen sulphite.

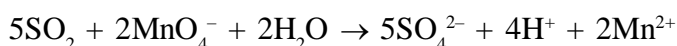
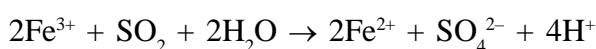


In its reaction with water and alkalis, the behaviour of sulphur dioxide is very similar to that of carbon dioxide. Sulphur dioxide reacts with chlorine in the presence of charcoal (which acts as a catalyst) to give sulphuryl chloride,  $\text{SO}_2\text{Cl}_2$ . It is oxidised to sulphur trioxide by oxygen in the presence of vanadium(V) oxide catalyst.

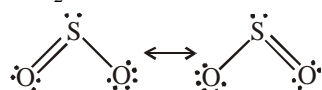


### Reducing properties

When moist, sulphur dioxide behaves as a reducing agent. For example, it converts iron(III) ions to iron(II) ions and decolourises acidified potassium permanganate(VII) solution; the latter reaction is a convenient test for the gas.



**Bonding in SO<sub>2</sub>** : The molecule of SO<sub>2</sub> is angular. It is a resonance hybrid of the two canonical forms:



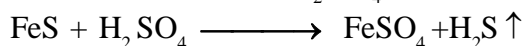
**Uses:**

- It is used refining petroleum and sugar
- It is used in bleaching wool and silk
- It is used as an anti-chlor, disinfectant and preservative. Sulphuric acid, sodium hydrogen sulphite and calcium hydrogen sulphite (industrial chemicals) are manufactured from sulphur dioxide. Liquid SO<sub>2</sub> is used as a solvent to dissolve a number of organic and inorganic chemicals.

### HYDROGEN SULPHIDE (H<sub>2</sub>S) SULPHURATED HYDROGEN

#### **Preparation**

By the action of dil. HCl or H<sub>2</sub>SO<sub>4</sub> on iron pyrites.

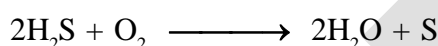


Note: **Drying agent for this gas : fused CaCl<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> (dehydrated) P<sub>2</sub>O<sub>5</sub> etc. But not H<sub>2</sub>SO<sub>4</sub>, because**  $\text{H}_2\text{SO}_4 + \text{H}_2\text{S} \longrightarrow 2\text{H}_2\text{O} + \text{SO}_2 + \text{S}$

#### **Properties**

It is a colourless gas having an offensive smell of rotten eggs.

- (a) It burn in air with blue flame



If the air supply is in excess



- (b) It is a mild acid.



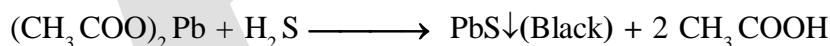
- (c) It act as a reducing agent. It reduces halogen into corresponding hydroacid.



#### **Tests of H<sub>2</sub>S**

- (a) Unpleasant odour resembling that of rotten eggs.

- (b) It turns lead acetate into paper black



- (c) It gives a violet colouration with a alkaline solution of sodium nitroprusside.

#### **Structure of H<sub>2</sub>S**

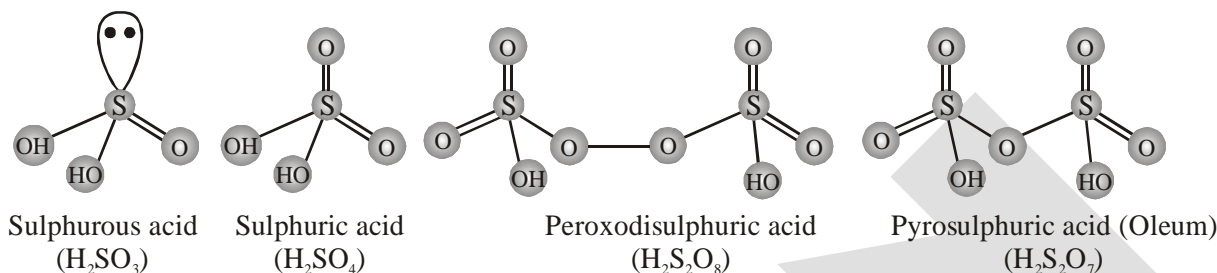
- (a) Similar to structure of water molecule i.e. V-shaped structure with bond length (H-S) 1.35Å and bond angle (H-S-H) is 92.5°

#### **Uses**

- It is mainly employed in salt analysis for the detection of cation.
- Reducing agent for H<sub>2</sub>SO<sub>4</sub>, KMnO<sub>4</sub>, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, FeCl<sub>3</sub>

## OXOACIDS OF SULPHUR

Sulphur forms a number of oxoacids such as  $\text{H}_2\text{SO}_3$ ,  $\text{H}_2\text{S}_2\text{O}_3$ ,  $\text{H}_2\text{S}_2\text{O}_4$ ,  $\text{H}_2\text{S}_2\text{O}_5$ ,  $\text{H}_2\text{S}_x\text{O}_6$  ( $x = 2$  to  $5$ ),  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{S}_2\text{O}_7$ ,  $\text{H}_2\text{SO}_5$ ,  $\text{H}_2\text{S}_2\text{O}_8$ . Some of these acids are unstable and cannot be isolated. They are known in aqueous solution or in the form of their salts. Structures of some important oxoacids are shown in Fig.



Structures of some important oxoacids of sulphur

## SULPHURIC ACID

Sulphuric acid is one of the most important industrial chemicals worldwide.

**Industrial Manufacturing** (Contact process)

Steps involved :

- (i) **Burning of sulphur or sulphide ores in air to generate  $\text{SO}_2$ .**
- (ii) **Conversion of  $\text{SO}_2$  to  $\text{SO}_3$  by the reaction with oxygen in the presence of a catalyst ( $\text{V}_2\text{O}_5$ ):**

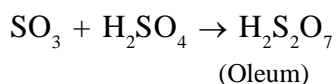
The  $\text{SO}_2$  produced is purified by removing dust and other impurities such as arsenic compounds. The key step in the manufacture of  $\text{H}_2\text{SO}_4$  is the catalytic oxidation of  $\text{SO}_2$  with  $\text{O}_2$  to give  $\text{SO}_3$  in the presence of  $\text{V}_2\text{O}_5$  (catalyst).

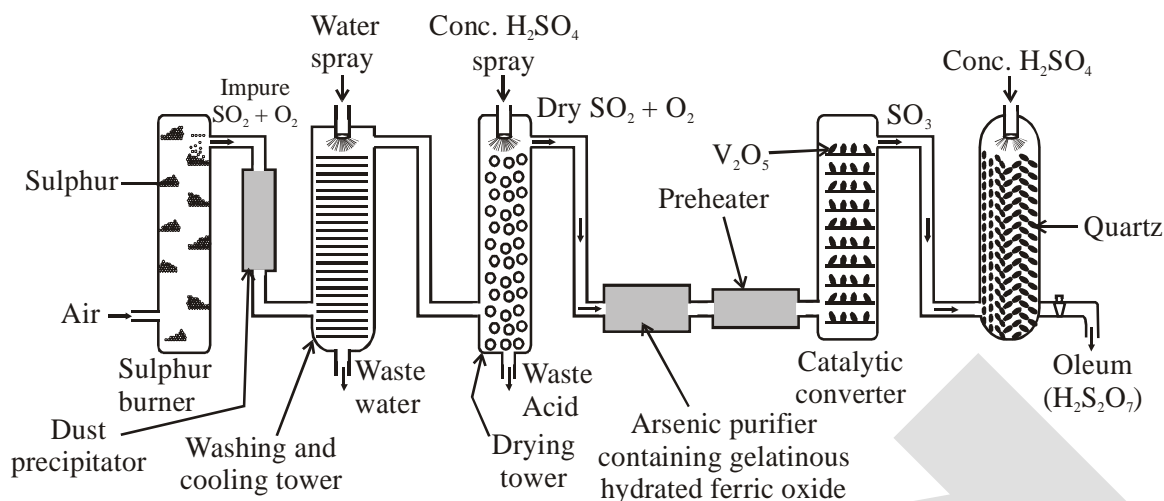


The reaction is exothermic, reversible and the forward reaction leads to a decrease in volume. Therefore, low temperature and high pressure are the favourable conditions for maximum yield. But the temperature should not be very low otherwise rate of reaction will become slow. In practice, the plant is operated at a pressure of 2 bar and a temperature of 720 K.

- (iii) **Absorption of  $\text{SO}_3$  in  $\text{H}_2\text{SO}_4$  to give Oleum ( $\text{H}_2\text{S}_2\text{O}_7$ ) :**

The  $\text{SO}_3$  gas from the catalytic converter is absorbed in concentrated  $\text{H}_2\text{SO}_4$  to produce oleum. Dilution of oleum with water gives  $\text{H}_2\text{SO}_4$  of the desired concentration. In the industry two steps are carried out simultaneously to make the process a continuous one and also to reduce the cost.





Flow diagram for the manufacture of sulphuric acid

The sulphuric acid obtained by Contact process is 96-98% pure.

$P_2O_5$  is stronger dehydrating agent than  $H_2SO_4$  :  $H_2SO_4 + P_2O_5 \longrightarrow 2HPO_3 + SO_3$

### Properties

- Sulphuric acid is a colourless, dense, oily liquid with a specific gravity of 1.84 at 298 K.
- The acid freezes at 283 K and boils at 611 K.
- It dissolves in water with the evolution of a large quantity of heat. Hence, care must be taken while preparing sulphuric acid solution from concentrated sulphuric acid. The concentrated acid must be added slowly into water with constant stirring.

### Chemical properties

The chemical reactions of sulphuric acid are as a result of the following characteristics:

- |                                   |                                           |
|-----------------------------------|-------------------------------------------|
| (a) low volatility                | (b) strong acidic character               |
| (c) strong affinity for water and | (d) ability to act as an oxidising agent. |

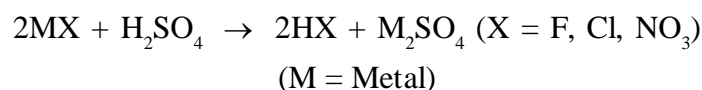
### Acidic character :

In aqueous solution, sulphuric acid ionises in two steps.



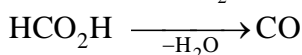
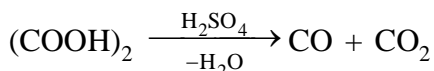
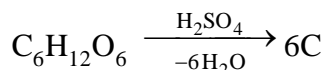
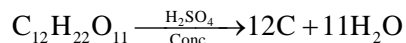
The larger value of  $K_{a_1}$  ( $K_{a_1} > 10$ ) means that  $H_2SO_4$  is largely dissociated into  $H^+$  and  $HSO_4^-$ . Greater the value of dissociation constant ( $K_a$ ), the stronger is the acid.

The acid forms two series of salts: normal sulphates (such as sodium sulphate and copper sulphate) and acid sulphates (e.g., sodium hydrogen sulphate). Sulphuric acid, because of its low volatility can be used to manufacture more volatile acids from their corresponding salts.

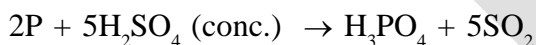
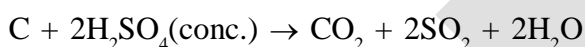
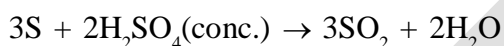
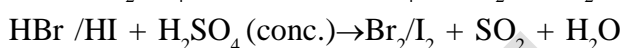
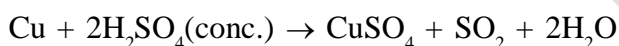
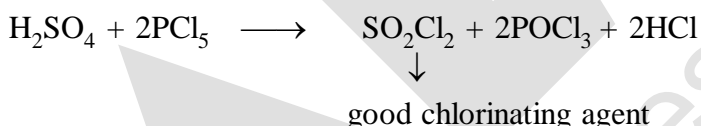
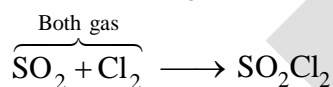


**Dehydrating Property :**

Concentrated sulphuric acid is a strong dehydrating agent. Many wet gases can be dried by passing them through sulphuric acid, provided the gases do not react with the acid. Sulphuric acid removes water from organic compounds; it is evident by its charring action on carbohydrates.

**Oxidizing Nature :**

Hot concentrated sulphuric acid is a moderately strong oxidising agent. In this respect, it is intermediate between phosphoric and nitric acids. Both metals and non-metals are oxidised by concentrated sulphuric acid, which is reduced to  $SO_2$ .

 **$H_2SO_4$  &  $SO_3$  :**

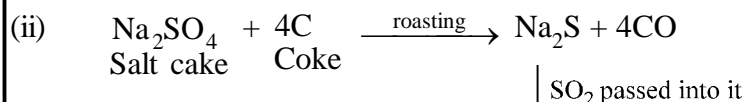
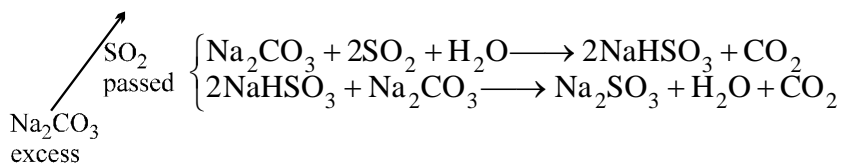
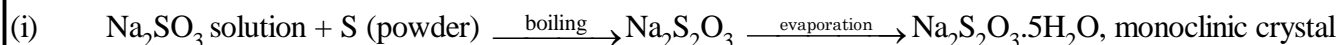
**Uses:** Sulphuric acid is a very important industrial chemical. A nation's industrial strength can be judged by the quantity of sulphuric acid it produces and consumes. It is needed for the manufacture of hundreds of other compounds and also in many industrial processes. The bulk of sulphuric acid produced is used in the manufacture of fertilisers (e.g., ammonium sulphate, superphosphate). Other uses are in:

- (i) petroleum refining
- (ii) manufacture of pigments, paints and dyestuff intermediates
- (iii) detergent industry
- (iv) metallurgical applications (e.g., cleansing metals before enameling, electroplating and galvanising)
- (v) storage batteries
- (vi) in the manufacture of nitrocellulose products and
- (vii) as a laboratory reagent.

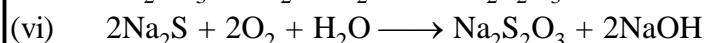
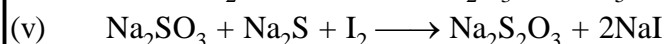
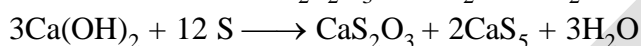
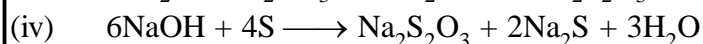
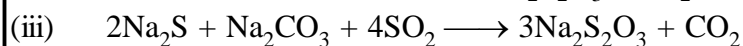
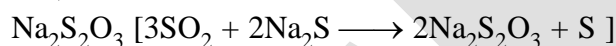


### SODIUM THIOSULPHATE

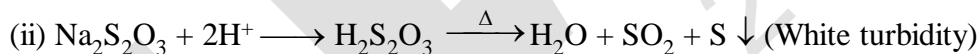
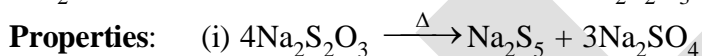
#### Preparation:



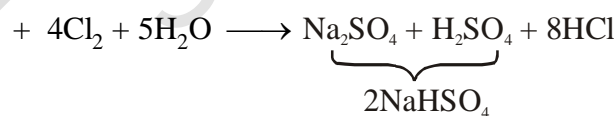
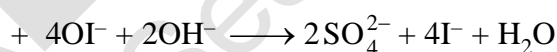
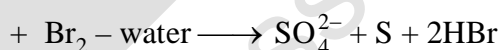
$\downarrow$   $\text{SO}_2$  passed into it



[ $\text{Na}_2\text{S}$  is readily oxidised in air giving rise to  $\text{Na}_2\text{S}_2\text{O}_3$ ]



#### Reaction:



## HALOGEN FAMILY

### GROUP 17 ELEMENTS (F, Cl, Br, I, At)

These are collectively known as the halogens (Greek halo means salt and genes means born i.e., salt producers). Astatine is a radioactive element.

#### ❑ Occurrence

- (i) Fluorine and chlorine are fairly abundant while bromine and iodine less so.
- (ii) Fluorine is present mainly as insoluble fluorides (fluorspar  $\text{CaF}_2$ , cryolite  $\text{Na}_3\text{AlF}_6$  and fluoroapatite  $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$ ) and small quantities are present in soil, river water plants and bones and teeth of animals.
- (iii) Sea water contains chlorides, bromides and iodides of sodium, potassium, magnesium and calcium, but is mainly sodium chloride solution (2.5% by mass).
- (iv) The deposits of dried up seas contain these compounds, e.g., sodium chloride and carnallite,  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . Certain forms of marine life contain iodine in their systems; various seaweeds, for example, contain upto 0.5% of iodine and Chile saltpetre contains upto 0.2% of sodium iodate.

#### Electronic Configuration

The electronic configuration of outermost shell 17<sup>th</sup> group element is  $(\text{ns}^2\text{np}^5)$ .

#### ❑ Atomic and ionic radii : $\text{F} < \text{Cl} < \text{Br} < \text{I}$

#### ❑ Ionisation Enthalpy : $\text{F} > \text{Cl} > \text{Br} > \text{I}$

#### ❑ Most Negative Electron Gain Enthalpy: $\text{Cl} > \text{F} > \text{Br} > \text{I}$

It is due to small size of fluorine atom. As a result, there are strong interelectronic repulsions in the relatively small 2p orbitals of fluorine and thus, the incoming electron does not experience much attraction.

#### ❑ Electronegativity : $\text{F} > \text{Cl} > \text{Br} > \text{I}$

#### ❑ Physical Properties

- (i) Their melting and boiling points steadily increase with atomic number.
- (ii) All halogens are coloured. For example,  $\text{F}_2$  is a yellow gas,  $\text{Cl}_2$  greenish yellow gas,  $\text{Br}_2$  red liquid and  $\text{I}_2$  violet coloured solid. Reason : Decrease in HOMO-LUMO gap.
- (iii) Fluorine and chlorine react with water. Bromine and iodine are only sparingly soluble in water but are soluble in various organic solvents such as chloroform, carbon tetrachloride, carbon disulphide and hydrocarbons to give coloured solutions.
- (iv) **Bond energy order ;  $\text{Cl}_2 > \text{Br}_2 > \text{F}_2 > \text{I}_2$**

A reason for this anomaly is the relatively large electron-electron repulsion among the lone pairs in  $\text{F}_2$  molecule where they are much closer to each other than in case of  $\text{Cl}_2$ .

## Chemical Properties

### Oxidation states :

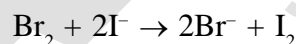
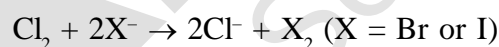
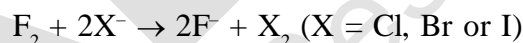
- (i) All the halogens exhibit  $-1$  oxidation state. However, chlorine, bromine and iodine exhibit  $+1$ ,  $+3$ ,  $+5$  and  $+7$  oxidation states also as explained below:

| Halogen atom<br>in ground state<br>(other than fluorine) | ns                   | np                                             | nd                                        |                                                                   |
|----------------------------------------------------------|----------------------|------------------------------------------------|-------------------------------------------|-------------------------------------------------------------------|
|                                                          | $\uparrow\downarrow$ | $\uparrow\downarrow\uparrow\downarrow\uparrow$ | $\square\square\square\square\square$     | 1 unpaired electron accounts<br>for $-1$ or $+1$ oxidation states |
| First excited state                                      | $\uparrow\downarrow$ | $\uparrow\downarrow\uparrow\uparrow\uparrow$   | $\uparrow\square\square\square\square$    | 3 unpaired electron accounts<br>for $+3$ oxidation states         |
| Second excited state                                     | $\uparrow\downarrow$ | $\uparrow\uparrow\uparrow\uparrow$             | $\uparrow\uparrow\square\square\square$   | 5 unpaired electron accounts<br>for $+5$ oxidation states         |
| Third excited state                                      | $\uparrow$           | $\uparrow\uparrow\uparrow\uparrow$             | $\uparrow\uparrow\uparrow\uparrow\square$ | 7 unpaired electron accounts<br>for $+7$ oxidation states         |

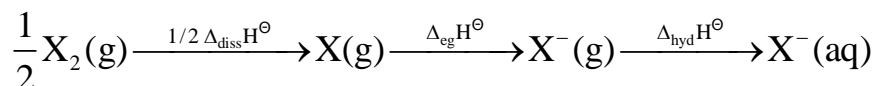
- (ii) The higher oxidation states of chlorine, bromine and iodine are realised mainly when the halogens are in combination with the small and highly electronegative fluorine and oxygen atoms. e.g., in interhalogens, oxides and oxoacids.
- (iii) The oxidation states of  $+4$  and  $+6$  occur in the oxides and oxoacids of chlorine and bromine.
- (iv) The fluorine atom has no d orbitals in its valence shell and therefore cannot expand its octet. Being the most electronegative, it exhibits only  $-1$  oxidation state.

### Chemical reactivity

- (i) All the halogens are highly reactive.
- (ii) They react with metals and non-metals to form halides and the reactivity of the halogens decreases down the group. i.e. the order is  $F_2 > Cl_2 > Br_2 > I_2$
- (iii) The ready acceptance of an electron is the reason for the strong oxidising nature of halogens.  $F_2$  is the strongest oxidising halogen and it oxidises other halide ions in solution or even in the solid phase. In general, a halogen oxidises halide ions of higher atomic number.

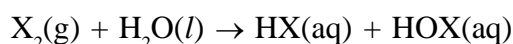
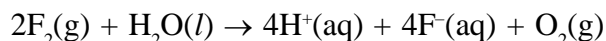


The decreasing oxidising ability of the halogens in aqueous solution down the group is evident from their standard electrode potentials, which are dependent on the parameters as follows :

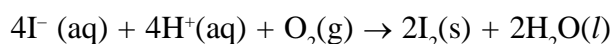


#### (1) Reactivity towards water

The relative oxidising power of halogens can further be illustrated by their reactions with water. Fluorine oxidises water to oxygen whereas chlorine and bromine react with water to form corresponding hydrohalic and hypohalous acids. The reaction of iodine with water is nonspontaneous. In fact,  $I^-$  can be oxidised by oxygen in acidic medium; just the reverse of the reaction is observed with fluorine.



(where X = Cl or Br)



### Note : Anomalous behaviour of fluorine

- (i) Fluorine is anomalous in many properties. For example, ionisation enthalpy, electronegativity, and electrode potentials are all higher for fluorine than expected from the trends set by other halogens. Also, ionic and covalent radii, m.p. and b.p., enthalpy of bond dissociation and electron gain enthalpy are quite lower than expected.
- (ii) Most of the reactions of fluorine are exothermic (due to the small and strong bond formed by it with other elements).
- (iii) It forms only one oxoacid while other halogens form a number of oxoacids.
- (iv) Hydrogen fluoride is a liquid (b.p. 293 K) due to strong hydrogen bonding. Other hydrogen halides are gases.

### Reason for the anomalous behaviour of fluorine

The anomalous behaviour of fluorine is due to its small size, highest electronegativity, low F-F bond dissociation enthalpy, and non availability of d orbitals in valence shell.

Properties of Hydrogen Halides

| Property                                                  | HF   | HCl   | HBr   | HI     |
|-----------------------------------------------------------|------|-------|-------|--------|
| Melting point/K                                           | 190  | 159   | 185   | 222    |
| Boiling point/K                                           | 293  | 189   | 206   | 238    |
| Bond length (H – X)/pm                                    | 91.7 | 127.4 | 141.4 | 160.9  |
| $\Delta_{\text{diss}}\text{H}^\ominus/\text{kJ mol}^{-1}$ | 57.4 | 432   | 363   | 295    |
| $\text{pK}_\text{a}$                                      | 3.2  | – 7.0 | – 9.5 | – 10.0 |

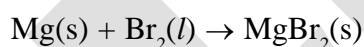
- (2) **Reactivity towards hydrogen :** They all react with hydrogen to give hydrogen halides but affinity for hydrogen decreases from fluorine to iodine. Hydrogen halides dissolve in water to form hydrohalic acids. Some of the properties of hydrogen halides are :

- (i) The acidic strength order :  $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$
- (ii) The stability order of these halides :  $\text{H-F} > \text{H-Cl} > \text{H-Br} > \text{H-I}$ .

- (3) **Reactivity towards oxygen :**

- (i) Halogens form many oxides with oxygen but most of them are unstable. Fluorine forms two oxides  $\text{OF}_2$  and  $\text{O}_2\text{F}_2$ . However, only  $\text{OF}_2$  is thermally stable at 298 K. These oxides are essentially oxygen fluorides because of the higher electronegativity of fluorine than oxygen. Both are strong fluorinating agents.  $\text{O}_2\text{F}_2$  oxidises plutonium to  $\text{PuF}_6$  and the reaction is used in removing plutonium as  $\text{PuF}_6$  from spent nuclear fuel.

- (ii) Chlorine, bromine and iodine form oxides in which the oxidation states of these halogens range from +1 to +7.
  - (iii) A combination of kinetic and thermodynamic factors lead to the generally decreasing order of stability of oxides formed by halogens,  $I > Cl > Br$ .
  - (iv) The higher oxides of halogens tend to be more stable than the lower ones.
  - (v) Chlorine oxides,  $Cl_2O$ ,  $ClO_2$ ,  $Cl_2O_6$  and  $Cl_2O_7$  are highly reactive oxidising agents and tend to explode.  $ClO_2$  is used as a bleaching agent for paper pulp and textiles and in water treatment.
  - (vi) The bromine oxides,  $Br_2O$ ,  $BrO_2$ ,  $BrO_3$  are the least stable halogen oxides (middle row anomaly) and exist only at low temperatures. They are very powerful oxidising agents.
  - (vii) The iodine oxides,  $I_2O_4$ ,  $I_2O_5$ ,  $I_2O_7$  are insoluble solids and decompose on heating.  $I_2O_5$  is a very good oxidising agent and is used in the estimation of carbon monoxide.
- (4) **Reactivity towards metals :** Halogens react with metals to form metal halides. For example, bromine reacts with magnesium to give magnesium bromide.



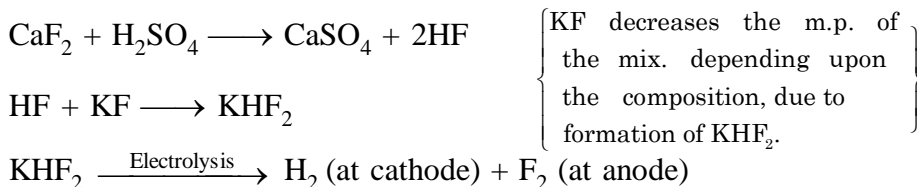
The ionic character of the halides decreases in the order  $MF > MCl > MBr > MI$  where M is monovalent metal. If a metal exhibits more than one oxidation state, the halides in higher oxidation state will be more covalent than the one in lower oxidation state. For example,  $SnCl_4$ ,  $PbCl_4$ ,  $SbCl_5$  and  $UF_6$  are more covalent than  $SnCl_2$ ,  $PbCl_2$ ,  $SbCl_3$  and  $UF_4$  respectively.

- (5) **Reactivity of halogens towards other halogens :** Halogens combine amongst themselves to form a number of compounds known as interhalogens of the types  $XX'$ ,  $XX_3'$ ,  $XX_5'$  and  $XX_7'$  where X is a larger size halogen and X' is smaller size halogen.

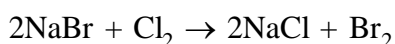
## FLUORINE

## Method of Preparation :

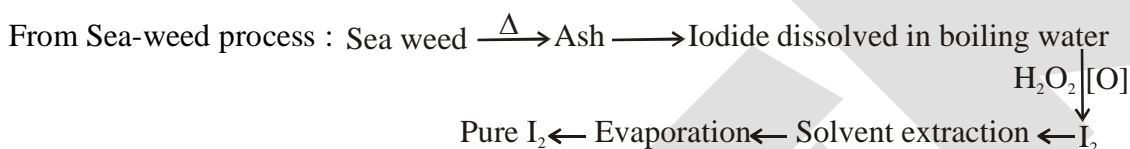
**Moissan process :** [By electrolysis of  $\text{KHF}_2$  (which is obtained from  $\text{CaF}_2$ )]



## BROMINE



## IODINE



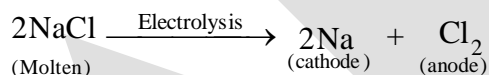
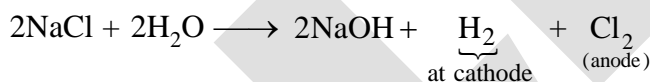
## CHLORINE

Chlorine was discovered in 1774 by Scheele by the action of  $\text{HCl}$  on  $\text{MnO}_2$ .

In 1810 Davy established its elementary nature and suggested the name chlorine on account of its colour (Greek, chloros = greenish yellow).

## Preparation

(i) By electrolysis of aq.  $\text{NaCl}$  :



(ii) By heating manganese dioxide with concentrated hydrochloric acid.



However, a mixture of common salt and concentrated  $\text{H}_2\text{SO}_4$  is used in place of  $\text{HCl}$ .

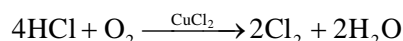


(iii) By the action of  $\text{HCl}$  on potassium permanganate.



□ **Manufacture of chlorine**

(i) **Deacon's process :** By oxidation of hydrogen chloride gas by atmospheric oxygen in the presence of  $\text{CuCl}_2$  (catalyst) at 723 K.

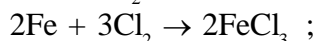
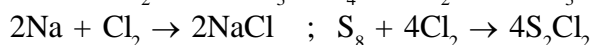
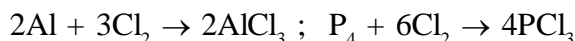


(ii) **Electrolytic process :** Chlorine is obtained by the electrolysis of brine (concentrated  $\text{NaCl}$  solution). Chlorine is liberated at anode. It is also obtained as a by-product in many chemical industries.

## Properties

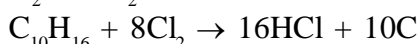
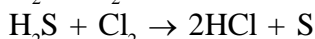
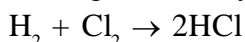
(i) It is a greenish yellow gas with pungent and suffocating odour.

- (ii) It is about 2-5 times heavier than air.  
 (iii) It can be liquefied easily into greenish yellow liquid which boils at 239 K.  
 (iv) It is soluble in water. Chlorine reacts with a number of metals and non-metals to form chlorides.



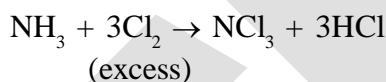
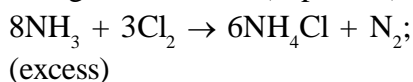
### Reaction with hydrogen

It has great affinity for hydrogen. It reacts with compounds containing hydrogen to form HCl.



### Reaction with ammonia

With excess ammonia, chlorine gives nitrogen and ammonium chloride whereas with excess chlorine, nitrogen trichloride (explosive) is formed.

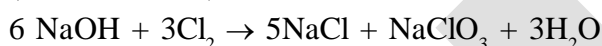


### Reaction with alkalis

With cold and dilute alkalis chlorine produces a mixture of chloride and hypochlorite but with hot and concentrated alkalis it gives chloride and chlorate.

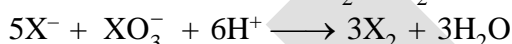
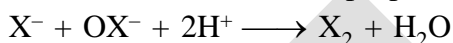


(cold and dilute)



(hot and conc.)

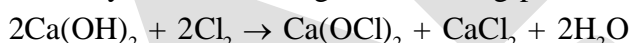
but on acidification the disproportionated product gives back the same element.



[X = Cl, Br, I]

### Reaction with slaked lime

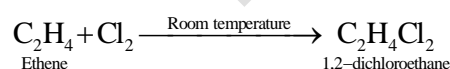
With dry slaked lime it gives bleaching powder.



The composition of bleaching powder is  $\text{Ca(OCl)}_2 \cdot \text{CaCl}_2 \cdot \text{Ca(OH)}_2 \cdot 2\text{H}_2\text{O}$ .

### Reaction with hydrocarbon

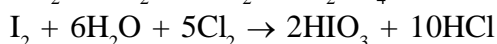
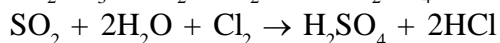
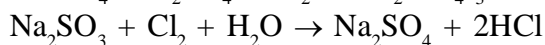
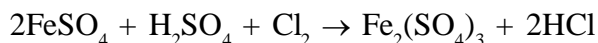
Chlorine reacts with hydrocarbons and gives substitution products with saturated hydrocarbons and addition products with unsaturated hydrocarbons. For example,



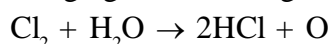
### Note :

Chlorine water on standing loses its yellow colour due to the formation of HCl and HOCl. Hypochlorous acid (HOCl) so formed, gives nascent oxygen which is responsible for oxidising and bleaching properties of chlorine.

- (i) It oxidises ferrous to ferric and sulphite to sulphate. Chlorine oxidises sulphur dioxide to sulphur trioxide and iodine to iodate. In the presence of water they form sulphuric acid and iodic acid respectively.



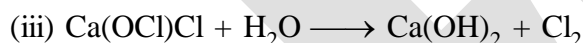
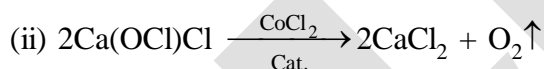
- (ii) It is a powerful bleaching agent; bleaching action is due to oxidation.


$$\text{Coloured substance} + \text{O} \rightarrow \text{Colourless substance}$$

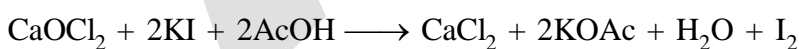
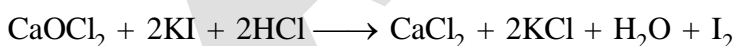
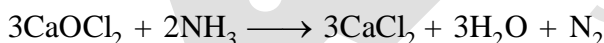
**Uses:** It is used (i) for bleaching woodpulp (required for the manufacture of paper and rayon), bleaching cotton and textiles, (ii) in the extraction of gold and platinum (iii) in the manufacture of dyes, drugs and organic compounds such as  $\text{CCl}_4$ ,  $\text{CHCl}_3$ , DDT, refrigerants, etc. (iv) in sterilising drinking water and (v) preparation of poisonous gases such as phosgene ( $\text{COCl}_2$ ), tear gas ( $\text{CCl}_3\text{NO}_2$ ), mustard gas ( $\text{ClCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{Cl}$ ). (vi) It bleaches vegetable or organic matter in the presence of moisture. Bleaching effect of chlorine is permanent.



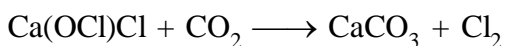
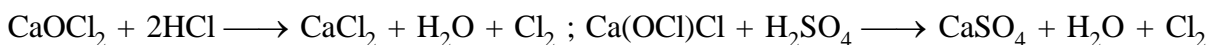
- (a) On long standing it undergoes



### Oxidising Properties:



**Reaction with acid:**



**Note:**  $\text{ClO}_2$  does not dimerise because odd electron undergoes delocalisation (in its own vacant 3d-orbital)



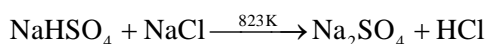
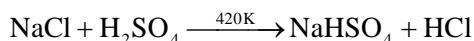


## HYDROGEN CHLORIDE

- (i) Glauber prepared this acid in 1648 by heating common salt with concentrated sulphuric acid.  
 (ii) Davy in 1810 showed that it is a compound of hydrogen and chlorine.

**Preparation**

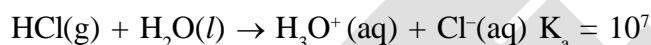
**Laboratory method** : it is prepared by heating sodium chloride with concentrated sulphuric acid.



HCl gas can be dried by passing through concentrated sulphuric acid.

**Properties**

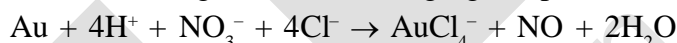
- (i) It is a colourless and pungent smelling gas. Due to strong affinity for water, conc. HCl pulls moisture of air towards self. The moisture forms droplets of water and hence, cloudy white fumes appear.  
 (ii) It is easily liquefied to a colourless liquid (b.p. 189 K) and freezes to a white crystalline solid (f.p. 159 K).  
 (iii) It is extremely soluble in water  
 (iv) **Acidic character** : It ionises as follows



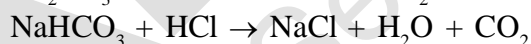
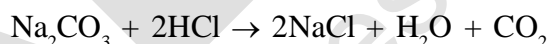
Its aqueous solution is called hydrochloric acid. High value of dissociation constant ( $K_a$ ) indicates that it is a strong acid in water. It reacts with  $\text{NH}_3$  and gives white fumes of  $\text{NH}_4\text{Cl}$ .

**Note : Aqua regia**

When three parts of concentrated HCl and one part of concentrated  $\text{HNO}_3$  are mixed, aqua regia is formed which is used for dissolving noble metals, e.g., gold, platinum.

**Reaction with salts**

Hydrochloric acid decomposes salts of weaker acids, e.g., carbonates, hydrogencarbonates, sulphites, etc.

**Uses:**

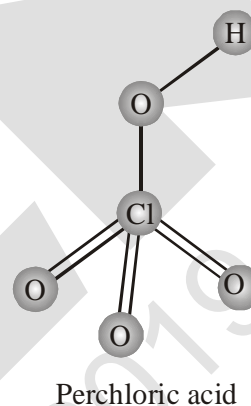
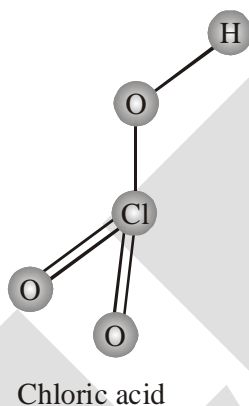
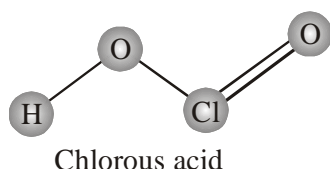
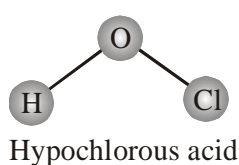
- (i) It is used in the manufacture of chlorine,  $\text{NH}_4\text{Cl}$  and glucose (from corn starch)  
 (ii) It is used for extracting glue from bones and purifying bone black  
 (iii) It is used in medicine and as a laboratory reagent.

## OXOACIDS OF HALOGENS

- (i) Due to high electronegativity and small size, fluorine forms only one oxoacid, HOF known as fluoric (I) acid or hypofluorous acid.  
 (ii) The other halogens form several oxoacids.  
 (iii) Most of them cannot be isolated in pure state. They are stable only in aqueous solutions or in the form of their salts.

## Oxoacids of Halogens

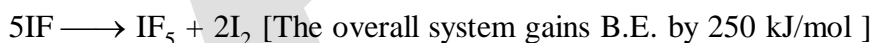
| <b>Halic (I) acid</b><br>(Hypohalous acid) | <b>HOX</b><br>(HypoXalous acid) | <b>HOXO</b><br>(HypoXalous acid)             | <b>HOXO</b><br>(HypoXalous acid)            | <b>HOXO</b><br>(HypoXalous acid)           |
|--------------------------------------------|---------------------------------|----------------------------------------------|---------------------------------------------|--------------------------------------------|
| <b>Halic (III) acid</b><br>(Halous acid)   | —                               | <b>HOXO</b><br>(Chlorous acid)               | —                                           | —                                          |
| <b>Halic (V) acid</b><br>(Halic acid)      | —                               | <b>HOXO<sub>2</sub></b><br>(Chloric acid)    | <b>HOXO<sub>2</sub></b><br>(Bromic acid)    | <b>HOXO<sub>2</sub></b><br>(Iodic acid)    |
| <b>Halic (VII) acid</b><br>(Perhalic acid) | —                               | <b>HOXO<sub>3</sub></b><br>(Perchloric acid) | <b>HOXO<sub>3</sub></b><br>(Perbromic acid) | <b>HOXO<sub>3</sub></b><br>(Periodic acid) |



The structures of oxoacids of chlorine

## INTERHALOGEN COMPOUNDS

When two different halogens react with each other, interhalogen compounds are formed. They can be assigned general compositions as  $XX'$ ,  $XX'_3$ ,  $XX'_5$  and  $XX'_7$  where X is halogen of larger size and X' of smaller size and X is more electropositive than X'. As the ratio between radii of X and X' increases, the number of atoms per molecule also increases. Thus, iodine (VII) fluoride should have maximum number of atoms as the ratio of radii between I and F should be maximum. That is why its formula is  $IF_7$  (having maximum number of atoms).



There are never more than two halogens in a molecule.

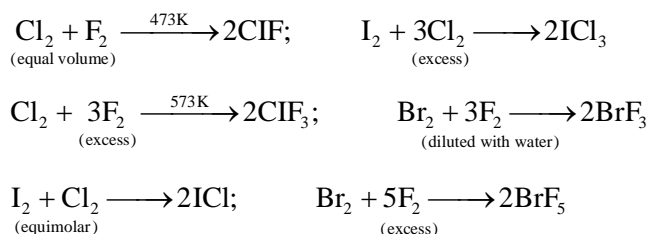
Bonds are essentially covalent and b.p. increases as the E.N. difference increases.

$AX_5$  &  $AX_7$  type formed by large atoms like Br & I to accommodate more atoms around it.

The interhalogens are generally more reactive than the halogens (except  $F_2$ ) due to weaker A–X bonds compared to X–X bond.

### Preparation

The interhalogen compounds can be prepared by the direct combination or by the action of halogen on lower interhalogen compounds. The product formed depends upon some specific conditions, For e.g.,



### Properties

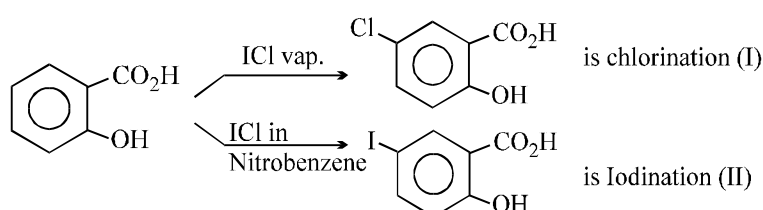
Some properties of interhalogen compounds are given in Table below

Some Properties of Interhalogen Compounds

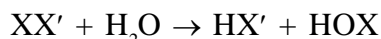
| Type           | Formula                   | Physical state and colour           | Structure              |
|----------------|---------------------------|-------------------------------------|------------------------|
| $\text{XX}'_1$ | $\text{ClF}$              | colourless gas                      | —                      |
|                | $\text{BrF}$              | pale brown gas                      | —                      |
|                | $\text{IF}^{\text{a}}$    | Detected spectroscopically          | —                      |
|                | $\text{BrCl}^{\text{b}}$  | gas                                 | —                      |
|                | $\text{ICl}$              | ruby red solid ( $\alpha$ -form)    | —                      |
| $\text{XX}'_3$ |                           | brown red solid ( $\beta$ -form)    | —                      |
|                | $\text{IBr}$              | black solid                         | —                      |
|                | $\text{ClF}_3$            | colourless gas                      | Bent T-shaped          |
|                | $\text{BrF}_3$            | yellow green liquid                 | Bent T-shaped          |
|                | $\text{IF}_3$             | yellow powder                       | Bent T-shaped          |
| $\text{Xx}'_5$ | $\text{ICl}_3^{\text{c}}$ | orange solid                        | Bent T-shaped          |
|                | $\text{IF}_5$             | colourless gas but solid below 77 K | square pyramidal       |
|                | $\text{BrF}_5$            | colourless liquid                   | square pyramidal       |
|                | $\text{ClF}_5$            | colourless liquid                   | square pyramidal       |
|                | $\text{IF}_7$             | colourless gas                      | pentagonal bipyramidal |

<sup>a</sup>Very unstable; <sup>b</sup>The pure solid is known at room temperature; <sup>c</sup>Dimerises as Cl-bridged dimer ( $\text{I}_2\text{Cl}_6$ )

### One peculiarity with $\text{ICl}$ :



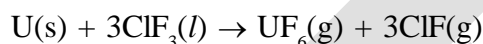
- (i) These are all covalent molecules and are diamagnetic in nature.
- (ii) They are volatile solids or liquids at 298 K except  $\text{ClF}$  which is a gas.
- (iii) Their physical properties are intermediate between those of constituent halogens except that their m.p. and b.p. are a little higher than expected.
- (iv) Their chemical reactions can be compared with the individual halogens. In general, interhalogen compounds are more reactive than halogens (except fluorine). This is because  $\text{X-X'}$  bond in interhalogens is weaker than  $\text{X-X}$  bond in halogens except  $\text{F-F}$  bond.
- (v) All these undergo hydrolysis giving halide ion derived from the smaller halogen and a hypohalite (when  $\text{XX'}$ ), halite (when  $\text{XX'_3}$ ), halate (when  $\text{XX'_5}$ ) and perhalate (when  $\text{XX'_7}$ ) anion derived from the larger halogen.



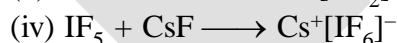
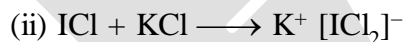
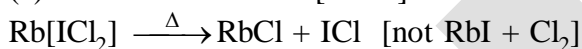
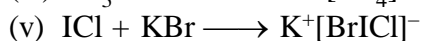
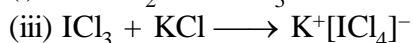
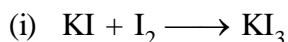
Their molecular structures are very interesting which can be explained on the basis of VSEPR theory. The  $\text{XX}_3$  compounds have the bent 'T' shape,  $\text{XX}_5$  compounds square pyramidal and  $\text{IF}_7$  has pentagonal bipyramidal structures.

**Uses:** (i) These compounds can be used as non aqueous solvents.

(ii) Interhalogen compounds are very useful fluorinating agents.  $\text{ClF}_3$  and  $\text{BrF}_3$  are used for the production of  $\text{UF}_6$  in the enrichment of  $^{235}\text{U}$ .

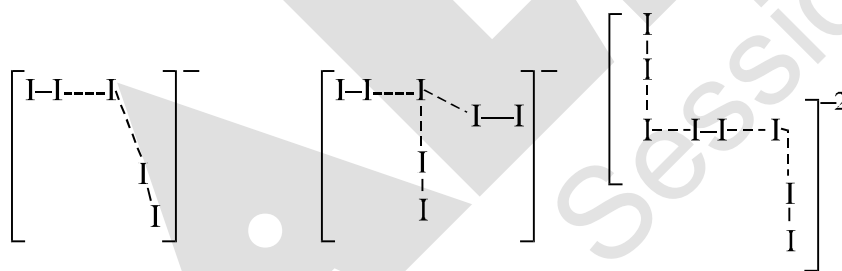


### POLYHALIDES



Here the products on heating depends on the lattice energy of the product halide. The lattice energy of alkali halide with smaller halogen is highest since the interatomic distance is least.

Structure of  $\text{I}_5^-$ ,  $\text{I}_7^-$ ,  $\text{I}_8^{2-}$



in  $[\text{N}(\text{CH}_3)_4]^+ \text{I}_7^-$  in  $\text{Cs}_2\text{I}_8$

$\text{I}_3^-$ ,  $\text{Br}_3^-$ ,  $\text{Cl}_3^-$ ,  $\text{F}_3^-$  are known  $\text{Cl}_3^-$  compounds are very less.

Stability order :  $\text{I}_3^- > \text{Br}_3^- > \text{Cl}_3^- > \text{F}_3^-$  depends upon the donating ability of  $\text{X}^-$ .

## PSEUDO HALOGENS

There are univalent ion consisting of two or more atoms of which at least one is N, that have properties similar to those of the halide ions. E.g.

- (i) Na-salts are soluble in water but Ag-salts are insoluble in water.  
 (ii) H-compounds are acids like HX. (iii) Some anions can be oxidised to give molecules  $X_2$ .

| Anions :              | Acids                   | Dimer      |
|-----------------------|-------------------------|------------|
| $CN^-$                | HCN                     | $(CN)_2$   |
| $SCN^-$               | HSCN(thiocyanic acid)   | $(SCN)_2$  |
| $SeCN^-$              |                         | $(SeCN)_2$ |
| $OCN^-$               | HOCN (cyanic acid)      |            |
| $NCN^{2-}$ (Bivalent) | $H_2NCN$ (cyanamide)    |            |
| $ONC^-$               | HONC (Fulminic acid)    |            |
| $N_3^-$               | $HN_3$ (Hydrazoic acid) |            |

$CN^\ominus$  shows maximum similarities with  $Cl^-$ ,  $Br^-$ ,  $I^-$

- (i) forms HCN (ii) forms  $(CN)_2$  (iii) AgCN,  $Pb(CN)_2$ , are insoluble  
 (iv) Interpseudo halogen compounds ClCN, BrCN, ICN can be formed  
 (v) AgCN is insoluble in  $H_2O$  but soluble in  $NH_3$   
 (vi) forms large no. of complexes. e.g.  $[Cu(CN)_4]^{3-}$  &  $[CuCl_4]^{3-}$   
 $[Co(CN)_6]^{3-}$  &  $[CoCl_6]^{3-}$

## NOBLE GASES FAMILY

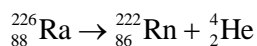
## GROUP 18 ELEMENTS (He, Ne, Ar, Kr, Xe, Rn)

## Occurrence

- (i) All the noble gases except radon occur in the atmosphere.

Relative abundance : Ar is highest (Ne, Kr, He, Rn)

- (ii) Their atmospheric abundance in dry air is ~ 1% by volume of which argon is the major constituent.  
 (iii) Helium and sometimes neon are found in minerals of radioactive origin e.g., pitchblende, monazite, cleveite.  
 (iv) The main commercial source of helium is natural gas.  
 (v) Xenon and radon are the rarest elements of the group.  
 (vi) Radon is obtained as a decay product of  $^{226}\text{Ra}$ .



- (vii) He liquid can exist in two forms. I-form when changes to II-form at  $\lambda$ -point temperature many physical properties change abruptly.

e.g.

- (i) Sp. heat changes by a factor of 10  
 (ii) Thermal conductivity increases by  $10^6$  and it becomes 800 times faster than Cu  
 (iii) It shows zero resistance  
 (iv) It can flow up the sides of the vessel

**Qus. Why 18 group element are termed as noble gas ?**

**Ans.** All these are gases and chemically unreactive. They form very few compounds. Because of this they are termed noble gases.

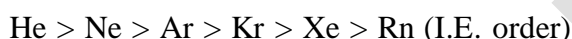
❑ **Electronic Configuration**

General electronic configuration of 18 group element is  $ns^2np^6$  except helium which has  $1s^2$ .

Many of the properties of noble gases including their inactive nature are ascribed to their closed shell structures.

❑ **Ionisation Enthalpy**

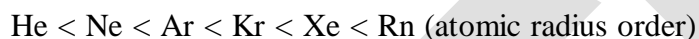
Ionisation energy decreases down the group with increase in atomic size.



Due to stable electronic configuration these gases exhibit very high ionisation enthalpy.

❑ **Atomic Radii**

Atomic radii increase down the group with increase in atomic number.



❑ **Electron Gain Enthalpy**

They have large positive values of electron gain enthalpy due to stable electronic configurations, and therefore have no tendency to accept the electron

❑ **Melting point and boiling point**

$\text{He} < \text{Ne} < \text{Ar} < \text{Kr} < \text{Xe} < \text{Rn}$  (Melting point order)

↓

( $-269^\circ\text{C}$ )

**B.P. order :**  $\text{He} < \text{Ne} < \text{Ar} < \text{Kr} < \text{Xe} < \text{Rn}$  (Boiling point order)

❑ **Density order :**



**Physical properties :**

(i) All the noble gases are monoatomic.

(ii) They are colourless, odourless and tasteless.

(iii) They are sparingly soluble in water.

(iv) They have very low melting and boiling points because the only type of interatomic interaction in these elements is weak dispersion forces.

(v) Helium has the lowest boiling point (4.2 K) of any known substance.

(vi) It has an unusual property of diffusing through most commonly used laboratory materials such as rubber, glass or plastics.

### ❑ Chemical Properties

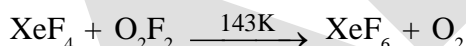
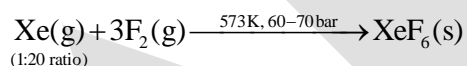
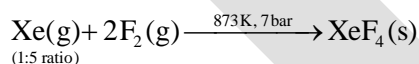
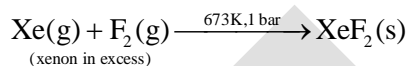
In general, noble gases are least reactive. Their inertness to chemical reactivity is attributed to the following reasons:

- (i) The noble gases except helium ( $1s^2$ ) have completely filled  $ns^2np^6$  electronic configuration in their valence shell.
- (ii) They have high ionisation enthalpy and more positive electron gain enthalpy.

**Note :** The reactivity of noble gases has been investigated occasionally. In March 1962, Neil Bartlett, then at the University of British Columbia, observed the reaction of a noble gas. First, he prepared a red compound which is formulated as  $O_2^+ PtF_6^-$ . He, then realised that the first ionisation enthalpy of molecular oxygen ( $1175 \text{ kJ mol}^{-1}$ ) was almost identical with that of xenon ( $1170 \text{ kJ mol}^{-1}$ ). He made efforts to prepare same type of compound with Xe and was successful in preparing another red colour compound  $Xe^+PtF_6^-$  by mixing  $PtF_6$  and xenon. After this discovery, a number of xenon compounds mainly with most electronegative elements like fluorine and oxygen, have been synthesised. The compounds of krypton are fewer. Only the difluoride ( $KrF_2$ ) has been studied in detail. Compounds of radon have not been isolated but only identified (e.g.,  $RnF_2$ ) by radiotracer technique. No true compounds of Ar, Ne or He are yet known.

### FLUORIDES OF XENON

#### Preparation

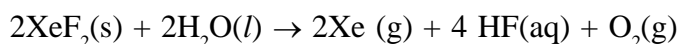


#### Physical properties

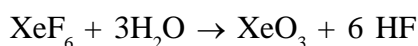
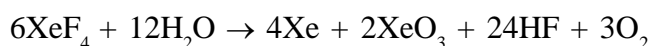
$XeF_2$ ,  $XeF_4$  and  $XeF_6$  are colourless crystalline solids and sublime readily at 298 K.

#### Chemical properties

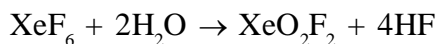
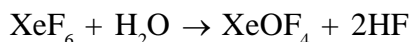
(i) **Hydrolysis :** They are readily hydrolysed even by traces of water. For example,  $XeF_2$  is hydrolysed to give Xe, HF and  $O_2$ .



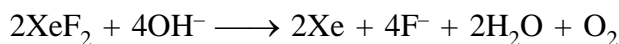
Hydrolysis of  $XeF_4$  and  $XeF_6$  with water gives  $XeO_3$ .



Partial hydrolysis of  $\text{XeF}_6$  gives oxyfluorides,  $\text{XeOF}_4$  and  $\text{XeO}_2\text{F}_2$ .



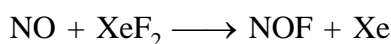
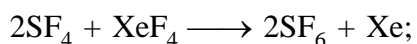
Note : **Hydrolysis in alkaline medium**



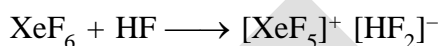
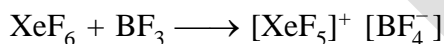
Xenate ion



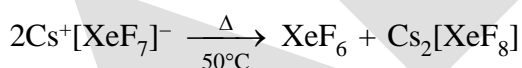
(ii) **As fluorinating agents** : They are powerful fluorinating agents.



(iii) **As fluoride donor**



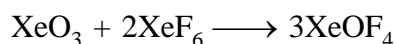
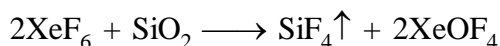
(iv) **As Fluoride acceptor**



(alkali metals fluoride)

(v) **Reaction with  $\text{SiO}_2$**

$\text{SiO}_2$  also converts  $\text{XeF}_6$  into  $\text{XeOF}_4$

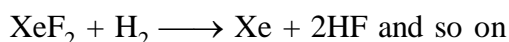


Similarly,  $\text{XeO}_3 + \text{XeOF}_4 \longrightarrow 2\text{XeO}_2\text{F}_2$

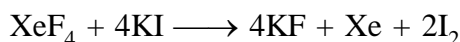
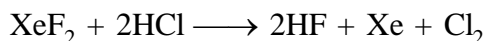


**(vi) Oxidizing properties**

H<sub>2</sub> reduces Xe – fluorides to Xe



Xe - fluorides oxidise Cl<sup>-</sup> to Cl<sub>2</sub> and I<sup>-</sup> to I<sub>2</sub>

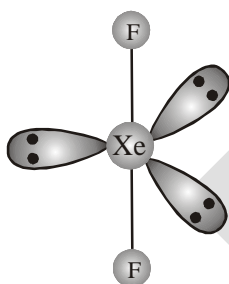


**Noble gas hydrate (clathrate compound) :** Ar, Kr, Xe can form clathrate compounds but He, Ne cannot due to their smaller size.

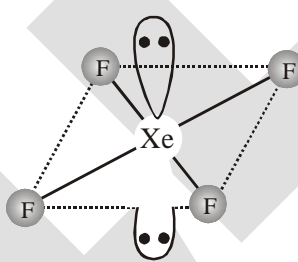
|                            |                                  |
|----------------------------|----------------------------------|
| eg. Xe • 6H <sub>2</sub> O | } formed only when               |
| Ar • 6H <sub>2</sub> O     |                                  |
| Kr • 6H <sub>2</sub> O     |                                  |
|                            | water freezes at high            |
|                            | pressure together with noble gas |

**(a) Structure and bonding**

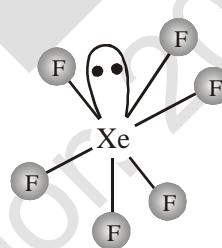
XeF<sub>2</sub> and XeF<sub>4</sub> have linear and square planar structures respectively. XeF<sub>6</sub> has seven electron pairs (6 bonding pairs and one lone pair) and would, thus, have a distorted octahedral structure as found experimentally in the gas phase. Xenon fluorides react with fluoride ion acceptors to form cationic species and fluoride ion donors to form fluoroanions.



(a) Linear



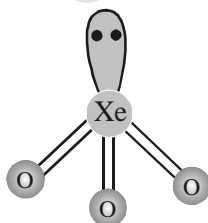
(b) Square planar



(c) Distorted octahedral

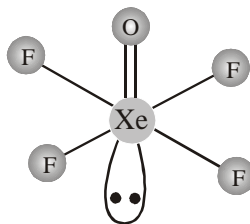
**(b) Xenon-oxygen compounds**

XeO<sub>3</sub> is a colourless, white hygroscopic explosive solid and has a pyramidal molecular structure.



Pyramidal

XeOF<sub>4</sub> is a colourless volatile liquid and has a square pyramidal molecular structure.



Square pyramidal

**Uses of helium :**

- (i) He is a non-inflammable and light gas. Hence, it is used in filling balloons for meteorological observations.
- (ii) It is also used in gas-cooled nuclear reactors.
- (iii) It is used in cryoscopy to obtain the very low temperature required for superconductor and laser (b.p. 4.2 K) finds use as cryogenic agent for carrying out various experiments at low temperatures.
- (iv) It is used to produce and sustain powerful superconducting magnets which form an essential part of modern NMR spectrometers and Magnetic Resonance Imaging (MRI) systems for clinical diagnosis.
- (v) It is used as a diluent for oxygen in modern diving apparatus because of its very low solubility in blood. He is used in preference to  $N_2$  to dil.  $O_2$  in the gas cylinders used by divers. This is because  $N_2$  is quite soluble in blood, so a sudden change in pressure causes degassing and gives bubbles of  $N_2$  in the blood. This causes the painful condition called bends. He is slightly soluble so the risk of bends is reduced.

**USES OF NEON :**

- (i) Ne is used in discharge tubes and fluorescent bulbs for advertisement display purposes.
- (ii) Neon bulbs are used in botanical gardens and in green houses.

**USES OF ARGON :**

- (i) Argon is used mainly to provide an inert atmosphere in high temperature metallurgical processes (arc welding of metals or alloys) and for filling electric bulbs.
- (ii) It is also used in the laboratory for handling substances that are air-sensitive.

**USES OF XENON AND KRYPTON :**

There are no significant uses of Xenon and Krypton. They are used in light bulbs designed for special purposes.

SOLVED EXAMPLE

1. Though nitrogen exhibits +5 oxidation state, it does not form pentahalide. Give reason.

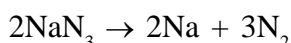
**Sol.** Nitrogen with  $n = 2$ , has s and p orbitals only. It does not have d orbitals to expand its covalency beyond four. That is why it does not form pentahalide.

2.  $\text{PH}_3$  has lower boiling point than  $\text{NH}_3$ . Why?

**Sol.** Unlike  $\text{NH}_3$ ,  $\text{PH}_3$  molecules are not associated through hydrogen bonding in liquid state. That is why the boiling point of  $\text{PH}_3$  is lower than  $\text{NH}_3$ .

3. Write the reaction of thermal decomposition of sodium azide.

**Sol.** Thermal decomposition of sodium azide gives dinitrogen gas.

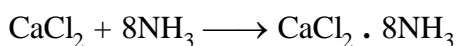
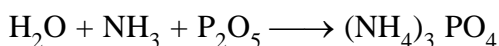


4. Why does  $\text{NH}_3$  act as a Lewis base ?

**Sol.** Nitrogen atom in  $\text{NH}_3$  has one lone pair of electrons which is available for donation. Therefore, it acts as a Lewis base.

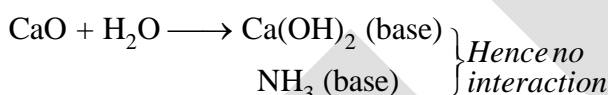
5.  $\text{NH}_3$  can't be dried by  $\text{H}_2\text{SO}_4$ ,  $\text{P}_2\text{O}_5$  and  $\text{anh. CaCl}_2$

**Sol.** because :  $2\text{NH}_3 + \text{H}_2\text{SO}_4 \longrightarrow (\text{NH}_4)_2 \text{SO}_4$



forms adduct

Quick lime is used for this purpose



$\text{NH}_3$  (base)

} Hence no interaction

6. Why does  $\text{NO}_2$  dimerise ?

**Sol.**  $\text{NO}_2$  contains odd number of valence electrons. It behaves as a typical odd molecule. On dimerisation, it is converted to stable  $\text{N}_2\text{O}_4$  molecule with even number of electrons.

7. In what way can it be proved that  $\text{PH}_3$  is basic in nature?

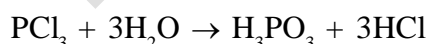
**Sol.**  $\text{PH}_3$  reacts with acids like HI to form  $\text{PH}_4\text{I}$  which shows that it is basic in nature.



Due to lone pair on phosphorus atom,  $\text{PH}_3$  is acting as a Lewis base in the above reaction.

8. Why does  $\text{PCl}_3$  fume in moisture ?

**Sol.**  $\text{PCl}_3$  hydrolyses in the presence of moisture giving fumes of HCl.



9. Are all the five bonds in  $\text{PCl}_5$  molecule equivalent? Justify your answer.

**Sol.**  $\text{PCl}_5$  has a trigonal bipyramidal structure and the three equatorial P-Cl bonds are equivalent, while the two axial bonds are different and longer than equatorial bonds.

10. How do you account for the reducing behaviour of  $\text{H}_3\text{PO}_2$  on the basis of its structure?

**Sol.** In  $\text{H}_3\text{PO}_2$ , two H atoms are bonded directly to P atom which imparts reducing character to the acid.

**11.** Elements of Group 16 generally show lower value of first ionisation enthalpy compared to the corresponding periods of group 15. Why?

**Sol.** Due to extra stable half-filled p orbitals electronic configurations of Group 15 elements, larger amount of energy is required to remove electrons compared to Group 16 elements.

**12.**  $\text{H}_2\text{S}$  is less acidic than  $\text{H}_2\text{Te}$ . Why?

**Sol.** Due to the decrease in bond (E–H) dissociation enthalpy down the group, acidic character increases.

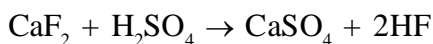
**13.** Which form of sulphur shows paramagnetic behaviour ?

**Sol.** In vapour state sulphur partly exists as  $\text{S}_2$  molecule which has two unpaired electrons in the antibonding  $\pi^*$  orbitals like  $\text{O}_2$  and, hence, exhibits paramagnetism.

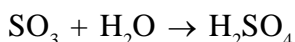
**14.** What happens when

- (i) Concentrated  $\text{H}_2\text{SO}_4$  is added to calcium fluoride
- (ii)  $\text{SO}_3$  is passed through water?

**Sol.** (i) It forms hydrogen fluoride



- (ii) It dissolves  $\text{SO}_3$  to give  $\text{H}_2\text{SO}_4$ .



**15.** Halogens have maximum negative electron gain enthalpy in the respective periods of the periodic table. Why?

**Sol.** Halogens have the smallest size in their respective periods and therefore high effective nuclear charge. As a consequence, they readily accept one electron to acquire noble gas electronic configuration.

**16.** Although electron gain enthalpy of fluorine is less negative as compared to chlorine, fluorine is a stronger oxidising agent than chlorine. Why?

**Sol.** It is due to

- (i) low enthalpy of dissociation of F–F bond
- (ii) high hydration enthalpy of  $\text{F}^-$

**17.** Fluorine exhibits only –1 oxidation state whereas other halogens exhibit +1, +3, +5 and +7 oxidation states also. Explain.

**Sol.** Fluorine is the most electronegative element and cannot exhibit any positive oxidation state. Other halogens have d orbitals and therefore, can expand their octets and show +1, +3, +5 and +7 oxidation states also.

**18.** Write the balanced chemical equation for the reaction of  $\text{Cl}_2$  with hot and concentrated  $\text{NaOH}$ . Is this reaction a disproportionation reaction? Justify.

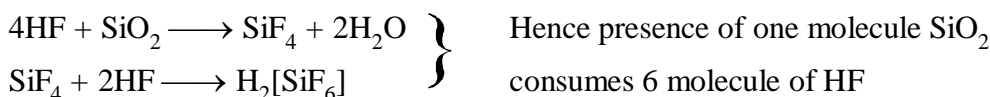
**Sol.**  $3\text{Cl}_2 + 6\text{NaOH} \rightarrow 5\text{NaCl} + \text{NaClO}_3 + 3\text{H}_2\text{O}$

Yes, chlorine from zero oxidation state is changed to –1 and +5 oxidation states.

**19.**  $\text{CaF}_2$  used in HF prep<sup>n</sup>. must be free from  $\text{SiO}_2$ . Explain.

**Ans.**  $\text{CaF}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{CaSO}_4 + \text{HF}$

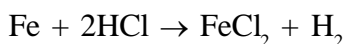
If  $\text{SiO}_2$  present as impurity



HF can not be stored in glass vessel due to same reason.

**20.** When HCl reacts with finely powdered iron, it forms ferrous chloride and not ferric chloride. Why?

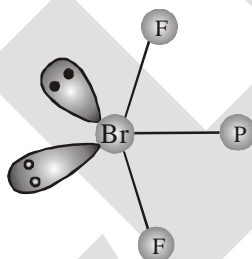
**Sol.** Its reaction with iron produces  $\text{H}_2$ .



Liberation of hydrogen prevents the formation of ferric chloride.

**21.** Discuss the molecular shape of  $\text{BrF}_3$  on the basis of VSEPR theory.

**Sol.** The central atom Br has seven electrons in the valence shell. Three of these will form electronpair bonds with three fluorine atoms leaving behind four electrons. Thus, there are three bond pairs and two lone pairs. According to VSEPR theory, these will occupy the corners of a trigonal bipyramid. The two lone pairs will occupy the equatorial positions to minimise lone pair-lone pair and the bond pair-lone pair repulsions which are greater than the bond pair-bond pair repulsions. In addition, the axial fluorine atoms will be bent towards the equatorial fluorine in order to minimise the lone-pair-lone pair repulsions. The shape would be that of a slightly bent 'T'.



**22.** Why are the elements of Group 18 known as noble gases ?

**Sol.** The elements present in Group 18 have their valence shell orbitals completely filled and, therefore, react with a few elements only under certain conditions. Therefore, they are now known as noble gases.

**23.** Noble gases have very low boiling points. Why?

**Sol.** Noble gases being monoatomic have no interatomic forces except weak dispersion forces and therefore, they are liquefied at very low temperatures. Hence, they have low boiling points.

**24.** Does the hydrolysis of  $\text{XeF}_6$  lead to a redox reaction?

**Sol.** No, the products of hydrolysis are  $\text{XeOF}_4$  and  $\text{XeO}_2\text{F}_2$  where the oxidation states of all the elements remain the same as it was in the reacting state.

**25.** Standard electrode potential values,  $E^\ominus$  for  $\text{Al}^{3+}/\text{Al}$  is  $-1.66\text{ V}$  and that of  $\text{Tl}^{3+}/\text{Tl}$  is  $+1.26\text{ V}$ . Predict about the formation of  $\text{M}^{3+}$  ion in solution and compare the electropositive character of the two metals.

**Sol.** Standard electrode potential values for two half cell reactions suggest that aluminium has high tendency to make  $\text{Al}^{3+}(\text{aq})$  ions, whereas  $\text{Tl}^{3+}$  is not only unstable in solution but is a powerful oxidising agent also. Thus  $\text{Tl}^+$  is more stable in solution than  $\text{Tl}^{3+}$ . Aluminium being able to form +3 ions easily, is more electropositive than thallium.

**26.** White fumes appear around the bottle of anhydrous aluminium chloride. Give reason.

**Sol.** Anhydrous aluminium chloride is partially hydrolysed with atmospheric moisture to liberate  $\text{HCl}$  gas. Moist  $\text{HCl}$  appears white in colour.

**27.** Boron is unable to form  $\text{BF}_6^{3-}$  ion. Explain.

**Sol.** Due to non-availability of d orbitals, boron is unable to expand its octet. Therefore, the maximum covalence of boron cannot exceed 4.

**28.** Why is boric acid considered as a weak acid ?

**Sol.** Because it is not able to release  $\text{H}^+$  ions on its own. It receives  $\text{OH}^-$  ions from water molecule to complete its octet and in turn releases  $\text{H}^+$  ions.

**29.** Select the member(s) of group 14 that (i) forms the most acidic dioxide, (ii) is commonly found in +2 oxidation state, (iii) used as semiconductor.

**Sol.** (i) carbon (ii) lead (iii) silicon and germanium

**30.**  $[\text{SiF}_6]^{2-}$  is known whereas  $[\text{SiCl}_6]^{2-}$  not. Give possible reasons.

**Sol.** The main reasons are :

(i) six large chloride ions cannot be accommodated around  $\text{Si}^{4+}$  due to limitation of its size.

(ii) interaction between lone pair of chloride ion and  $\text{Si}^{4+}$  is not very strong.

**31.** Diamond is covalent, yet it has high melting point. Why ?

**Sol.** Diamond has a three-dimensional network involving strong  $\text{C}-\text{C}$  bonds, which are very difficult to break and, in turn has high melting point.

**32.**  $\text{SiH}_4$  is more reactive than  $\text{CH}_4$ . Explain

#### Reasons

(i)  $\text{Si}^{\delta+} - \text{H}^{\delta-}$  in  $\text{C}^{\delta-} - \text{H}^{\delta+}$

C - more electronegative than H

Si less electronegative than H

So bond polarity is reversed when  $\text{Nu}^-$  attacks, it faces repulsion in C but not in Si

(ii) Silicon is having vacant d orbital which is not in case of carbon

(iii) Silicon is larger in size compared to C. By which the incoming  $\text{Nu}^-$  doesn't face any steric hindrance to attack at Si whereas  $\text{CH}_4$  is tightly held from all sides.

## EXERCISE # I

Only one option is correct :

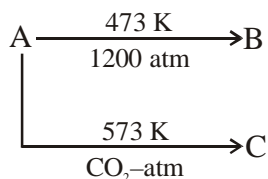
1.  $\text{PH}_3$  (Phosphine) when passed in aqueous solution of  $\text{CuSO}_4$  it produce -  
 (A) Blue precipitate of  $\text{Cu}(\text{OH})_2$  (B) dark blue solution of  $[\text{Cu}(\text{PH}_3)_4]\text{SO}_4$   
 (C) Black precipitate of  $\text{Cu}_3\text{P}_2$  (D) Colorless solution of  $[\text{Cu}(\text{H}_2\text{O})_4]^+$
2.  $\text{H}_3\text{PO}_2 \xrightarrow{\Delta} (\text{X}) + \text{PH}_3$  ; is  
 (A) Dehydration reaction (B) Oxidation reaction  
 (C) Disproportionation reaction (D) Dephosphorelation reaction
3. Which of the following species is not a pseudohalide?  
 (A)  $\text{CNO}^-$  (B)  $\text{RCOO}^-$  (C)  $\text{OCN}^-$  (D)  $\text{N}_3^-$
4. An orange solid (X) on heating, gives a colourless gas (Y) and a only green residue (Z). Gas (Y) on treatment with Mg, produces a white solid substance .....  
 (A)  $\text{Mg}_3\text{N}_2$  (B)  $\text{MgO}$  (C)  $\text{Mg}_2\text{O}_3$  (D)  $\text{MgCl}_2$
5. Conc.  $\text{HNO}_3$  is yellow coloured liquid due to  
 (A) dissolution of NO in conc.  $\text{HNO}_3$  (B) dissolution of  $\text{NO}_2$  in conc.  $\text{HNO}_3$   
 (C) dissolution of  $\text{N}_2\text{O}$  in conc.  $\text{HNO}_3$  (D) dissolution of  $\text{N}_2\text{O}_3$  in conc.  $\text{HNO}_3$
6. A gas at low temperature does not react with the most of compounds. It is almost inert and is used to create inert atmosphere in bulbs. The combustion of this gas is exceptionally an endothermic reaction. Based on the given information, we can conclude that the gas is  
 (A) oxygen (B) nitrogen  
 (C) carbon mono-oxide (D) hydrogen
7. When chlorine gas is passed through an aqueous solution of a potassium halide in the presence of chloroform, a violet colouration is obtained. On passing more of chlorine water, the violet colour is disappeared and solution becomes colourless. This test confirms the presence of ..... in aqueous solution.  
 (A) chlorine (B) fluorine (C) bromine (D) iodine
8.  $\text{H}_3\text{PO}_2 \xrightarrow{140^\circ\text{C}} \text{A} \xrightarrow{220^\circ\text{C}} \text{B} \xrightarrow{320^\circ\text{C}} \text{C}$   
 Compound (C) is  
 (A)  $\text{H}_2\text{PO}_3$  (B)  $\text{H}_3\text{PO}_3$  (C)  $(\text{HPO}_3)_n$  (D)  $\text{H}_4\text{P}_2\text{O}_7$
9. An explosive compound (A) reacts with water to produce  $\text{NH}_4\text{OH}$  and  $\text{HOCl}$ . Then, the compound (A), is  
 (A) TNG (B)  $\text{NCl}_3$  (C)  $\text{PCl}_3$  (D)  $\text{HNO}_3$
10. An inorganic compound (A) made of two most occurring elements into the earth crust, having a polymeric tetrahedral network structure. With carbon, compound (A) produces a poisonous gas (B) which is the most stable diatomic molecule. Compounds (A) and (B) will be  
 (A)  $\text{SiO}_2$ ,  $\text{CO}_2$  (B)  $\text{SiO}_2$ , CO (C) SiC, CO (D)  $\text{SiO}_2$ ,  $\text{N}_2$

11. A sulphate of a metal (A) on heating evolves two gases (B) and (C) and an oxide (D). Gas (B) turns  $K_2Cr_2O_7$  paper green while gas (C) forms a trimer in which there is no S–S bond. Compound (D) with HCl, forms a Lewis acid (E) which exists as a dimer. Compounds (A), (B), (C), (D) and (E) are respectively  
 (A)  $FeSO_4$ ,  $SO_2$ ,  $SO_3$ ,  $Fe_2O_3$ ,  $FeCl_3$  (B)  $Al_2(SO_4)_3$ ,  $SO_2$ ,  $SO_3$ ,  $Al_2O_3$ ,  $FeCl_3$   
 (C)  $FeS$ ,  $SO_2$ ,  $SO_3$ ,  $FeSO_4$ ,  $FeCl_3$  (D)  $FeS$ ,  $SO_2$ ,  $SO_3$ ,  $Fe_2(PO_4)_3$ ,  $FeCl_2$
12. A tetra-atomic molecule (A) on reaction with nitrogen(I)oxide, produces two substances (B) and (C). (B) is a dehydrating agent while substance (C) is a diatomic gas which shows almost inert behaviour. The substances (A) and (B) and (C) respectively will be  
 (A)  $P_4$ ,  $P_4O_{10}$ ,  $N_2$  (B)  $P_4$ ,  $N_2O_5$ ,  $N_2$  (C)  $P_4$ ,  $P_2O_3$ , Ar (D)  $P_4$ ,  $P_2O_3$ ,  $H_2$
13. First compound of inert gases was prepared by scientist Neil Bartlett in 1962. This compound is  
 (A)  $XePtF_6$  (B)  $XeO_3$  (C)  $XeF_6$  (D)  $XeOF_4$
14. Carbongene has X% of  $CO_2$  and is used as an antidote for poisoning of Y. Then, X and Y are  
 (A) X = 95% and Y = lead poisoning (B) X = 5% and Y = CO poisoning  
 (C) X = 30% and Y =  $CO_2$  poisoning (D) X = 45% and Y = CO poisoning
15. The correct order of acidic strength of oxides of nitrogen is  
 (A)  $NO < NO_2 < N_2O < N_2O_3 < N_2O_5$  (B)  $N_2O < NO < N_2O_3 < N_2O_4 < N_2O_5$   
 (C)  $NO < N_2O < N_2O_3 < N_2O_5 < N_2O_4$  (D)  $NO < N_2O < N_2O_5 < N_2O_3 < N_2O_4$
16.  $H_3BO_3 \xrightarrow{T_1} X \xrightarrow{T_2} Y \xrightarrow{\text{red hot}} B_2O_3$   
 if  $T_1 < T_2$  then X and Y respectively are  
 (A) X = Metaboric acid and Y = Tetraboric acid  
 (B) X = Tetraboric acid and Y = Metaboric acid  
 (C) X = Borax and Y = Metaboric acid  
 (D) X = Tetraboric acid and Y = Borax
17. When conc.  $H_2SO_4$  was treated with  $K_4[Fe(CN)_6]$ , CO gas was evolved. By mistake, somebody used dilute  $H_2SO_4$  instead of conc.  $H_2SO_4$  then the gas evolved was  
 (A) CO (B) HCN (C)  $N_2$  (D)  $CO_2$
18. An inorganic white crystalline compound (A) has a rock salt structure. (A) on reaction with conc.  $H_2SO_4$  and  $MnO_2$ , evolves a pungent smelling, greenish-yellow gas (B). Compound (A) gives white ppt. of (C) with  $AgNO_3$  solution. Compounds (A), (B) and (C) will be respectively  
 (A) NaCl,  $Cl_2$ , AgCl (B) NaBr,  $Br_2$ , NaBr  
 (C) NaCl,  $Cl_2$ ,  $Ag_2SO_4$  (D)  $Na_2CO_3$ ,  $CO_2$ ,  $Ag_2CO_3$
19.  $RCl \xrightarrow[Si]{Cu\text{-powder}} R_2SiCl_2 \xrightarrow{H_2O} R_2Si(OH)_2 \xrightarrow{\text{condensation}} A$   
 Compound (A) is  
 (A) a linear silicone (B) a chlorosilane (C) a linear silane (D) a network silane

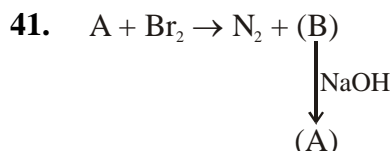


20. When oxalic acid reacts with conc.  $\text{H}_2\text{SO}_4$ , two gases produced are of neutral and acidic in nature respectively. Potassium hydroxide absorbs one of the two gases. The product formed during this absorption and the gas which gets absorbed are respectively
- (A)  $\text{K}_2\text{CO}_3$  and  $\text{CO}_2$  (B)  $\text{KHCO}_3$  and  $\text{CO}_2$   
 (C)  $\text{K}_2\text{CO}_3$  and  $\text{CO}$  (D)  $\text{KHCO}_3$  and  $\text{CO}$
21. Conc.  $\text{H}_2\text{SO}_4$  cannot be used to prepare  $\text{HBr}$  from  $\text{NaBr}$  because it
- (A) reacts slowly with  $\text{NaBr}$  (B) oxidises  $\text{HBr}$   
 (C) reduces  $\text{HBr}$  (D) disproportionates  $\text{HBr}$
22. Ammonia can be dried by
- (A) conc.  $\text{H}_2\text{SO}_4$  (B)  $\text{P}_4\text{O}_{10}$  (C)  $\text{CaO}$  (D) anhydrous  $\text{CaCl}_2$
23. When chlorine reacts with a gas X, an explosive inorganic compound Y is formed. Then X and Y will be
- (A)  $\text{X} = \text{O}_2$  and  $\text{Y} = \text{NCl}_3$  (B)  $\text{X} = \text{NH}_3$  and  $\text{Y} = \text{NCl}_3$   
 (C)  $\text{X} = \text{O}_2$  and  $\text{Y} = \text{NH}_4\text{Cl}$  (D)  $\text{X} = \text{NH}_3$  and  $\text{Y} = \text{NH}_4\text{Cl}$
24.  $\text{HNO}_3 + \text{P}_4\text{O}_{10} \longrightarrow \text{HPO}_3 + \text{A}$ ; the product A is
- (A)  $\text{N}_2\text{O}$  (B)  $\text{N}_2\text{O}_3$  (C)  $\text{NO}_2$  (D)  $\text{N}_2\text{O}_5$
25. Which of the following is the correct order of acidic strength?
- (A)  $\text{Cl}_2\text{O}_7 > \text{SO}_3 > \text{P}_4\text{O}_{10}$  (B)  $\text{CO}_2 > \text{N}_2\text{O}_5 > \text{SO}_3$   
 (C)  $\text{Na}_2\text{O} > \text{MgO} > \text{Al}_2\text{O}_3$  (D)  $\text{K}_2\text{O} > \text{CaO} > \text{MgO}$
26.  $\text{Ca} + \text{C}_2 \longrightarrow \text{CaC}_2 \xrightarrow{\text{N}_2} \text{A}$   
 Compound (A) is used as a/an
- (A) fertilizer (B) dehydrating agent (C) oxidising agent (D) reducing agent
27. A gas which exists in three allotropic forms  $\alpha$ ,  $\beta$  and  $\gamma$  is
- (A)  $\text{SO}_2$  (B)  $\text{SO}_3$  (C)  $\text{CO}_2$  (D)  $\text{NH}_3$
28. A red coloured mixed oxide (X) on treatment with conc.  $\text{HNO}_3$  gives a compound (Y). (Y) with  $\text{HCl}$ , produces a chloride compound (Z) which can also be produced by treating (X) with conc.  $\text{HCl}$ . Compounds (X), (Y), and (Z) will be
- (A)  $\text{Mn}_3\text{O}_4$ ,  $\text{MnO}_2$ ,  $\text{MnCl}_2$  (B)  $\text{Pb}_3\text{O}_4$ ,  $\text{PbO}_2$ ,  $\text{PbCl}_2$   
 (C)  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{FeCl}_2$  (D)  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{FeCl}_3$
29. One mole of calcium phosphide on reaction with excess of water gives
- (A) one mole of phosphine (B) two moles of phosphoric acid  
 (C) two moles of phosphine (D) one mole of phosphorus penta-oxide
30.  $\text{NaH}_2\text{PO}_4 \xrightarrow{> 240^\circ\text{C}} (\text{NaPO}_3)_3 \xrightarrow{625^\circ\text{C}} \text{NaPO}_3(\text{liquid melt}) \xrightarrow[\text{cooling}]{\text{rapid}} \text{D}(\text{glass})$   
 Sodium trimetaphosphate
- Compound (D) is known as
- (A) Microcosmic salt (B) Graham's salt (C) Fischer's salt (D) Switzer's Salt

31. Three allotropes (A), (B) and (C) of phosphorous in the following change are respectively



- (A) white,  $\beta$ -black, red (B)  $\beta$ -black, white, red  
 (C) red,  $\beta$ -black, white (D) red, violet,  $\beta$ -black
32. When an inorganic compound reacts with  $\text{SO}_2$  in aqueous medium, produces (A). (A) on reaction with  $\text{Na}_2\text{CO}_3$ , gives compound (B) which with sulphur, gives a substance (C) used in photography. Compound (C) is
- (A)  $\text{Na}_2\text{S}$  (B)  $\text{Na}_2\text{S}_2\text{O}_7$  (C)  $\text{Na}_2\text{SO}_4$  (D)  $\text{Na}_2\text{S}_2\text{O}_3$
33.  $\text{B(OH)}_3 + \text{NaOH} \rightleftharpoons \text{NaBO}_2 + \text{Na[B(OH)}_4] + \text{H}_2\text{O}$   
 How can this reaction is made to proceed in forward direction?
- (A) addition of cis 1,2 diol (B) addititon of borax  
 (C) addition of trans 1,2 diol (D) addition of  $\text{Na}_2\text{HPO}_4$
34. Which is the compound responsible for the flickering light called **will-o-the-wisp**, some times seen in the Marsh.
- (A)  $\text{PH}_3$  (B)  $\text{P}_2\text{H}_4$  (C)  $\text{H}_2\text{S}$  (D)  $\text{PH}_3 + \text{H}_2\text{S}$
35. The gun powder is consisting of '\_\_\_\_\_' + sulphur + Charcoal what is the missing substance for gun powder
- (A)  $\text{LiNO}_3$  (B)  $\text{NH}_4\text{NO}_2$  (C)  $\text{KNO}_3$  (D) (A) and (B) mixture
36. An aqueous solution of borax is
- (A) Neutral (B) Amphoteric (C) Basic (D) Acidic
37. Boric acid is polymeric due to
- (A) Its acidic nature  
 (B) The presence of hydrogen bonds  
 (C) Its monobasic nature  
 (D) Its geometry
38. The type of hybridisation of boron in diborane is
- (A) sp (B)  $\text{sp}^2$  (C)  $\text{sp}^3$  (D)  $\text{dsp}^2$
39. Thermodynamically the most stable form of carbon is
- (A) Diamond (B) Graphite (C) Fullerenes (D) Coal
40. Elements of group 14
- (A) Exhibit oxidation state of +4 only (B) Exhibit oxidation state of +2 and +4 only  
 (C) Form  $\text{M}^{2-}$  and  $\text{M}^{4+}$  ions (D) Form  $\text{M}^{2+}$  and  $\text{M}^{4+}$  ions



if A is a basic gas then identified (A) and (B)

- (A)  $NH_3$ ,  $NH_4Br$       (B)  $NH_3$ ,  $N_2O$       (C)  $NH_3$ ,  $N_2O_5$       (D) None of these

**Question No. 42 to 47 (6 questions)**

Questions given below consist of two statements each printed as Assertion (A) and Reason (R); while answering these questions you are required to choose any one of the following four responses:

- (A) if both (A) and (R) are true and (R) is the correct explanation of (A)  
 (B) if both (A) and (R) are true but (R) is not correct explanation of (A)  
 (C) if (A) is true but (R) is false  
 (D) if (A) is false and (R) is true

42. **Assertion :** Borax bead test is applicable only to coloured salt.

**Reason :** In borax bead test, coloured salts are decomposed to give coloured metal meta borates.

43. **Assertion :** Aluminium and zinc metal evolve  $H_2$  gas from NaOH solution

**Reason :** Several non-metals such as P, S, Cl, etc. convert a hydride instead of producing  $H_2$  gas from NaOH.

44. **Assertion :** Conc.  $H_2SO_4$  can not be used to prepare pure HBr from NaBr

**Reason :** It reacts slowly with NaBr.

45. **Assertion :** Oxygen is more electronegative than sulphur, yet  $H_2S$  is acidic, while  $H_2O$  is neutral.

**Reason :** H-S bond is weaker than O-H bond.

46. **Assertion :** Chlorine gas disproportionates in hot & conc. NaOH solution.

**Reason :** NaCl and NaOCl are formed in the above reaction.

47. **Assertion :** Liquid  $IF_5$  conducts electricity.

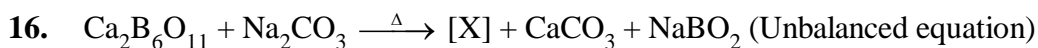
**Reason :** Liquid  $IF_5$  self ionizes as,  $2IF_5 \rightleftharpoons IF_4^+ + IF_6^-$

## EXERCISE # II

One or more than one option may be correct :

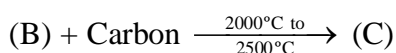
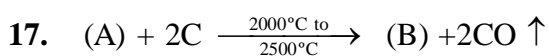
- When a compound X reacts with ozone in aqueous medium, a compound Y is produced. Ozone also reacts with Y and produces compound Z. Z acts as an oxidising agent, then X, Y and Z will be  
(A)  $X = \text{HI}$ ,  $Y = \text{I}_2$  and  $Z = \text{HIO}_3$   
(B)  $X = \text{KI}$ ,  $Y = \text{I}_2$  and  $Z = \text{HIO}_3$   
(C)  $X = \text{KI}$ ,  $Y = \text{I}_2$  and  $Z = \text{HIO}_4$   
(D)  $X = \text{HI}$ ,  $Y = \text{I}_2$  and  $Z = \text{HIO}_4$
- Which of the following statements is/are correct regarding  $\text{B}_2\text{H}_6$ ?  
(A) banana bonds are longer but stronger than normal B–H bonds  
(B)  $\text{B}_2\text{H}_6$  is also known as 3c–2e compound  
(C) the hybrid state of B in  $\text{B}_2\text{H}_6$  is  $\text{sp}^3$  while that of  $\text{sp}^2$  in  $\text{BH}_3$   
(D) it cannot be prepared by reacting  $\text{BF}_3$  with  $\text{LiBH}_4$  in the presence of dry ether
- Which of the following statements is/are correct regarding inter-halogen compounds of  $\text{AB}_x$  type?  
(A) x may be 1, 3, 5 and 7  
(B) A is a more electronegative halogen than B  
(C)  $\text{FBr}_3$  cannot exist  
(D) The interhalogens are generally more reactive than the halogens (except  $\text{F}_2$ ) due to weaker A–X bonds compared to X–X bond.
- When an inorganic compound (X) having 3c–2e as well as 2c–2e bonds reacts with ammonia gas at a certain temperature, gives a compound (Y) iso-structural with benzene. Compound (X) with ammonia at a high temperature, produces a slippery substance (Z). Then  
(A) (X) is  $\text{B}_2\text{H}_6$   
(B) (Z) is known as inorganic graphite  
(C) (Z) having structure similar to graphite  
(D) (Z) having structure similar to (X)
- Boric acid  
(A) exists in polymeric form due to inter-molecular hydrogen bonding.  
(B) is used in manufacturing of optical glasses.  
(C) is a tri-basic acid  
(D) with borax, it is used in the preparation of a buffer solution.

6. The correct statement(s) related to allotropes of carbon is/are
- (A) graphite is the thermodynamically most stable allotrope of carbon and having a two dimensional sheet like structure of hexagonal rings of carbon ( $sp^2$ )
- (B) diamond is the hardest allotrope of carbon and having a three dimensional network structure of  $C(sp^3)$
- (C) fullerene ( $C_{60}$ ) is recently discovered non-crystalline allotrope of carbon having a football-like structure.
- (D) Vander Waal's force of attraction acts between the layers of graphite  $6.14 \text{ \AA}$  away from each other
7.  $Al_2(SO_4)_3 + NH_4OH \longrightarrow X$ , then
- (A) X is a white coloured compound (B) X is insoluble in excess of  $NH_4OH$
- (C) X is soluble in NaOH (D) X cannot be used as an antacid
8. The species that undergo(es) disproportionation in an alkaline medium is/are
- (A)  $Cl_2$  (B)  $MnO_4^{2-}$  (C)  $P_4$  (D)  $ClO_4^-$
9. Select correct statement(s):
- (A) Borax is used as a buffer
- (B) 1 M borax solution reacts with equal volumes of 2 M HCl solution
- (C) Titration of borax can be made using methyl orange as the indicator
- (D) Coloured bead obtained in borax-bead test contains metaborate
10. Which of the following is / are correct for group 14 elements?
- (A) The stability of dihalides are in the order  $CX_2 < SiX_2 < GeX_2 < SnX_2 < PbX_2$
- (B) The ability to form  $p\pi-p\pi$  multiple bonds among themselves increases down the group
- (C) The tendency for catenation decreases down the group
- (D) They all form oxides with the formula  $MO_2$ .
11. Zeolite is used in which of the following cases :
- (A) Conversion of alcohols into gasoline (B) Cracking of hydrocarbon
- (C) Isomerisation of hydrocarbons (D) Softening of hard water
12. Which of the following oxides are mixed oxide ?
- (A)  $PbO_2$  (B)  $SnO_2$  (C)  $Pb_2O_3$  (D)  $Pb_3O_4$
13. Which of the following oxide(s) gives brown ppt on reaction with conc.  $HNO_3$  :
- (A)  $PbO$  (B)  $SnO$  (C)  $Pb_2O_3$  (D)  $Pb_3O_4$
14. Which of the following reaction produces  $PH_3$  :
- (A)  $Ca_3P_2 + H_2O \rightarrow$  (B)  $P_4 + NaOH \rightarrow$  (C)  $PH_4I + KOH \rightarrow$  (D)  $H_3PO_2 \xrightarrow{\Delta}$
15. Which of the following halides is least stable and has doubtful existence ?
- (A)  $CCl_4$  (B)  $GeI_4$  (C)  $SnI_4$  (D)  $PbI_4$



Correct statement for [X]

- (A) Structure of anion of crystalline (X) has one boron atom  $\text{sp}^3$  hybridised and other three boron atoms  $\text{sp}^2$  hybridised
- (B) (X) with  $\text{NaOH(aq.)}$  gives a compound which on reaction with  $\text{H}_2\text{O}_2$  in alkaline medium yields a compound used as brightner in soaps
- (C) Hydrolysis of (X) with  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$  yields a compound which on reaction with  $\text{HF}$  gives fluoroboric acid
- (D) [X] on heating with cobalt salt in oxidising flame gives blue coloured bead

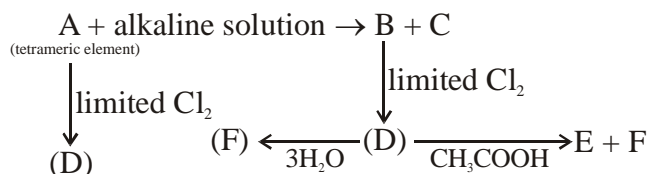


If A is an example of 3-d silicate then select the correct statements about (C)

- (A) Central atom of C is  $\text{sp}^3$  hybridised
- (B) (C) is non planar and all atoms are  $\text{sp}^3$  hybridised
- (C) (C) has diamond like structure, and it is coloured when impurity is present but pale yellow to colourless solid at room temperature
- (D) (C) is silicon carbide ( $\text{SiC}$ ) and it is not being affected by any acid except  $\text{H}_3\text{PO}_4$

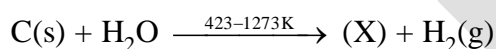
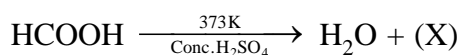
EXERCISE # III

Paragraph for Question No. 1 & 2



- When D react with  $\text{C}_2\text{H}_5\text{OH}$  then product will be  
 (A)  $\text{C}_2\text{H}_5\text{Cl}$ ,  $\text{H}_3\text{PO}_4$  (B)  $\text{C}_2\text{H}_5\text{Cl}$ ,  $\text{H}_3\text{PO}_3$   
 (C)  $\text{CH}_3\text{COCl}$ ,  $\text{H}_3\text{PO}_3$  (D) Only  $\text{H}_3\text{PO}_3$
- B can be absorbed by :  
 (A)  $\text{Ca}(\text{OCl})\text{Cl}$  (B)  $\text{H}_2\text{S}$  (C) Both (D) None

Paragraph for Question No. 3 to 6



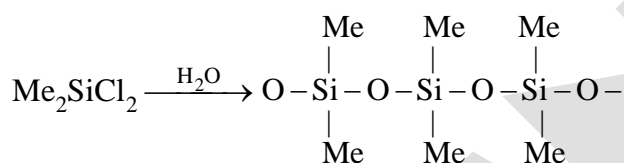
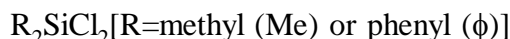
- Select the correct statement about (X)  
 (A) (X) is a colourless, odourless and almost water insoluble gas  
 (B) X is highly poisonous and burns with blue flame  
 (C) When (X) gas is passed through  $\text{PdCl}_2$  solution giving rise to black ppt  
 (D) All of these
- Mixture of (X) gas +  $\text{H}_2$  is called  
 (A) Water gas or synthesis gas (B) Producer gas  
 (C) Methane gas (D) None of these
- In second reaction when air is used instead of steam a mixture of (X) gas and  $\text{N}_2$  is produced which is called  
 (A) Water gas (B) Synthesis gas (C) Producer gas (D) Carbon dioxide gas
- Select the correct statement about (X)  
 (A) (X) gas is estimated by  $\text{I}_2\text{O}_5$  (B)  $\text{Cu}_2\text{Cl}_2$  is absorber of (X) gas  
 (C) (X) gas is the purifying agent for Ni (D) All of these

## Paragraph for Question No. 7 &amp; 8

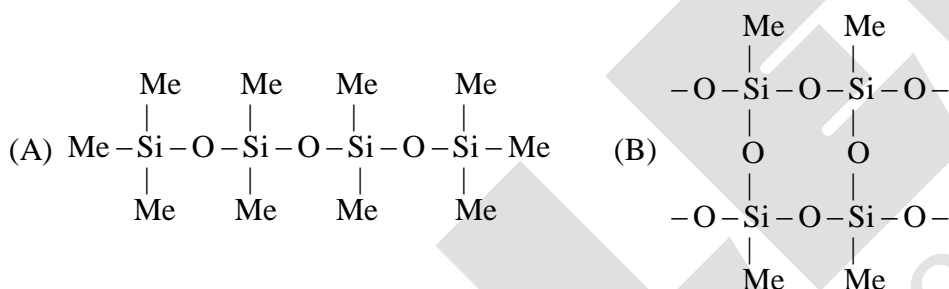
Read the following write-ups and answer the questions at the end of it.

Silicons are synthetic polymers containing repeated  $R_2SiO$  units. Since, the empirical formula is that of a ketone ( $R_2CO$ ), the name silicone has been given to these materials. Silicones can be made into oils, rubbery elastomers and resins. They find a variety of applications because of their chemical inertness, water repelling nature, heat-resistance and good electrical insulating property.

Commercial silicon polymers are usually methyl derivatives and to a lesser extent phenyl derivatives and are synthesised by the hydrolysis of



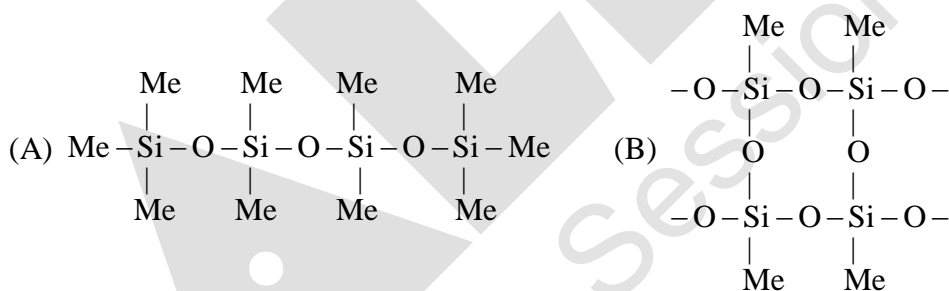
7. If we mix  $Me_3SiCl$  with  $Me_2SiCl_2$ , we get silicones of the type:



(C) both of the above

(D) none of the above

8. If we start with  $MeSiCl_3$  as the starting material, silicones formed is:



(C) Both of the above

(D) None of the above

## Paragraph for Question No. 9 &amp; 10

CO gas is absorbed by aqueous suspension of cuprous chloride forming the complex like  $[CuCl(CO)(H_2O)_2]$ .

9. Comment on the shape of the above complex.

(A) Tetrahedral

(B) TBP

(C) Square planar

(D) Cannot be predicted

10. Choose the correct statement regarding the above molecule

(A) Cl-atom is separated by equal angle from both of the water molecule

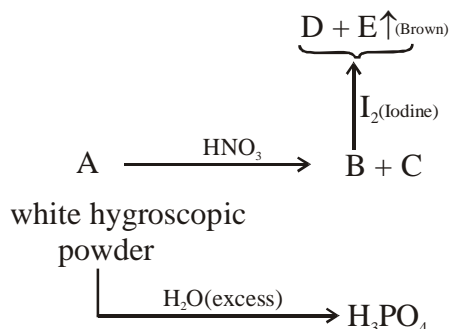
(B) Magnetic moment of the above complex is 1.73 B.M.

(C) There are two stereo isomer for the above complex.

(D) Both (A) and (C)



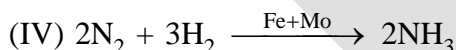
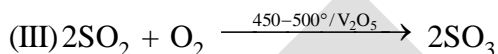
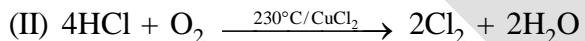
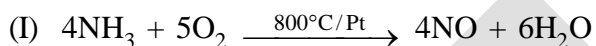
Paragraph for Question No. 11 to 12



11. Which of the following compound is not having +5 oxidation state on its central atom  
 (A) B (B) D (C) C (D) E
12. "A" on reacting with Acetamide yields a compound "F". The compound "F" contains  
 (A) 4  $\sigma$  bonds, 2  $\pi$  bonds  
 (B) 5  $\sigma$  bonds, 1  $\pi$  bonds  
 (C) 5  $\sigma$  bonds, 2  $\pi$  bonds  
 (D) 2  $\sigma$  bonds, 2  $\pi$  bonds

13. Match List-I with List-II

List-I (Chemical reaction)



(A) I-a, II-b, III-d, IV-c

(C) I-a, II-d, III-c, IV-b

List-II (Name of process)

(a) Contact process

(b) Ostwald's process

(c) Deacon's process

(d) Haber's process

(B) I-b, II-c, III-a, IV-d

(D) I-a, II-c, III-b, IV-d

14. Column-I

(P) Dry ice

(Q) Carbongene

(R) Carborundum

(S) Teflon

Column-II

(1) Used as antidote for CO-poisoning

(2) Used as nonstick coating

(3) Used as refrigerant

(4) Used as abrasive

Code :

|     | P | Q | R | S |
|-----|---|---|---|---|
| (A) | 4 | 1 | 3 | 2 |
| (C) | 3 | 1 | 4 | 2 |

|     | P | Q | R | S |
|-----|---|---|---|---|
| (B) | 4 | 2 | 1 | 3 |
| (D) | 1 | 4 | 3 | 2 |

## 15. Column-I

## Compound

- (P)  $\text{SnCl}_2$   
 (Q) Butter of tin  
 (R) Mosaic gold  
 (S) Pink's salt

## Code :

|     | P | Q | R | S |
|-----|---|---|---|---|
| (A) | 4 | 3 | 2 | 1 |
| (C) | 2 | 1 | 3 | 4 |

## Column-II

## Correct statement for compounds given

- (1) Used in printing technology  
 (2) Used for gilding purpose (in joining gold pieces)  
 (3) Reducing agent  
 (4) Mordant

|     | P | Q | R | S |
|-----|---|---|---|---|
| (B) | 3 | 4 | 2 | 1 |
| (D) | 1 | 3 | 4 | 2 |

## 16. Column-I (Metal)

- (P) Fe  
 (Q) Cu  
 (R) Pb  
 (S) Sn

## Code :

|     | P    | Q    | R    | S       |
|-----|------|------|------|---------|
| (A) | 2, 1 | 1    | 3, 4 | 2, 3    |
| (B) | 2, 3 | 1, 3 | 1, 3 | 2, 3, 4 |
| (C) | 1, 3 | 1, 2 | 3, 4 | 2       |
| (D) | 1, 4 | 2, 3 | 1, 3 | 1, 4    |

## Column-II (Correct statements)

- (1) Produces NO with 20%  $\text{HNO}_3$   
 (2) Produces  $\text{NH}_4\text{NO}_3$  with 6%  $\text{HNO}_3$   
 (3) Produces  $\text{NO}_2$  with 70%  $\text{HNO}_3$   
 (4) Produces  $\text{NH}_4\text{NO}_3$  with 20%  $\text{HNO}_3$

## 17. Column-I (Reactions)

- (P)  $\text{XeF}_2 + \text{PF}_5 \rightarrow$   
 (Q)  $\text{XeF}_4 + \text{Pt} \rightarrow$   
 (R)  $\text{XeF}_4 + \text{H}_2\text{O} \rightarrow$   
 (S)  $\text{XeF}_6 + \text{CsF} \rightarrow$

## Code :

|     | P | Q | R | S |
|-----|---|---|---|---|
| (A) | 4 | 2 | 3 | 1 |
| (C) | 4 | 3 | 2 | 1 |

## Column-II (Correct statements)

- (1) Fluoride of Xe acts as fluoride acceptor  
 (2) Fluoride of Xe undergoes disproportion  
 (3) Fluoride of Xe acts as fluorinating agent  
 (4) Fluoride of Xe act as fluoride donor

|     | P | Q | R | S |
|-----|---|---|---|---|
| (B) | 3 | 2 | 1 | 4 |
| (D) | 3 | 4 | 2 | 1 |

18. Column-I (Substances)

Column-II (Can be prepared by)

(P)  $O_3$

(1) Acidification of  $BaO_2$  with  $H_3PO_4$

(Q) Bleaching powder

(2) Birkeland Eyde process

(R)  $H_2O_2$

(3) Dry  $O_2$  is passed through a silent electrical discharge

(S)  $HNO_3$

(4)  $Cl_2$  gas is passed through slaked lime

Code :

|     | P | Q | R | S |
|-----|---|---|---|---|
| (A) | 3 | 4 | 1 | 2 |
| (C) | 2 | 1 | 3 | 4 |

|     | P | Q | R | S |
|-----|---|---|---|---|
| (B) | 1 | 3 | 4 | 2 |
| (D) | 4 | 1 | 2 | 3 |

**MATCHING LIST TYPE 1 × 3 Q. (19 to 21)**

For the following molecules in column-I, match the correct order of properties with column-II & column-III according to the questions asked.

| Column - 1<br>Molecules                   | Column - 2<br>Properties   | Column - 3<br>Correct order |
|-------------------------------------------|----------------------------|-----------------------------|
| (I) $NH_3$ , $PH_3$ , $AsH_3$ , $SbH_3$   | (i) Bond angle             | (p) Increasing order        |
| (II) $H_2O$ , $H_2S$ , $H_2Se$ , $H_2Te$  | (ii) Reducing character    | (q) Decreasing order        |
| (III) $HF$ , $HCl$ , $HBr$ , $HI$         | (iii) Intermolecular force | (r) All equal               |
| (IV) $CH_4$ , $SiH_4$ , $GeH_4$ , $SnH_4$ | (iv) Boiling Point         | (s) Irregular order         |

19. Which is the only **CORRECT** combination?

- (A) (I), (iv), (p)      (B) (II), (i), (p)      (C) (III), (iv), (q)      (D) (IV), (iii), (p)

20. Which is the only **INCORRECT** combination?

- (A) (I), (ii), (p)      (B) (IV), (i), (r)      (C) (III), (iii), (q)      (D) (II), (iv), (s)

21. In which combination, Drago's Rule plays an insignificant role in prediction of orders?

- (A) (I), (i), (q)      (B) (II), (iv), (s)      (C) (IV), (i), (r)      (D) (III), (ii), (p)

MATCHING LIST TYPE  $1 \times 3$  Q. (22 to 24)

| Molecule                           | Hybridization of central atom(s) | Properties related to structure                                                     |
|------------------------------------|----------------------------------|-------------------------------------------------------------------------------------|
| (P) $(\text{HBNH})_3$              | (I) $\text{sp}^2$                | (i) Cyclic structure                                                                |
| (Q) $\text{C}_3\text{O}_2$         | (II) $\text{sp}^3$               | (ii) Has $(\text{X}-\ddot{\text{O}}-\text{X})$ linkage ( $\text{X}$ = central atom) |
| (R) $\text{P}_4\text{O}_{12}^{4-}$ | (III) $\text{sp}^3\text{d}$      | (iii) Planar                                                                        |
| (S) $\text{N}_2\text{O}_4$         | (IV) $\text{sp}$                 | (iv) Has $(\text{X}-\text{X})$ linkage                                              |

22. Identify **CORRECT** match

(A) P, II, iii

(B) P, I, i

(C) P, IV, iii

(D) Q, I, i

23. Identify **CORRECT** match

(A) Q, IV, iii

(B) Q, IV, i

(C) Q, I, ii

(D) R, I, ii

24. Identify **CORRECT** match

(A) R, II, iv

(B) R, II, ii

(C) S, III, ii

(D) S, IV, i

## EXERCISE # JEE-MAINS

1. Which products are expected from the disproportionation of hypochlorous acid : [AIEEE-2002]  
(1)  $\text{HClO}_3$  and  $\text{Cl}_2\text{O}$  (2)  $\text{HClO}_2$  and  $\text{HClO}$  (3)  $\text{HCl}$  and  $\text{Cl}_2\text{O}$  (4)  $\text{HCl}$  and  $\text{HClO}_3$
2. Identify the **INCORRECT** statement among the following : [AIEEE-2002]  
(1) Ozone reacts with  $\text{SO}_2$  to give  $\text{SO}_3$   
(2) Silicon reacts with  $\text{NaOH(aq.)}$  in the presence of air to give  $\text{Na}_2\text{SiO}_3$  and  $\text{H}_2\text{O}$   
(3)  $\text{Cl}_2$  reacts with excess of  $\text{NH}_3$  to give  $\text{N}_2$  and  $\text{HCl}$   
(4)  $\text{Br}_2$  reacts with hot and strong  $\text{NaOH}$  solution to give  $\text{NaBr}$ ,  $\text{NaBrO}_4$  and  $\text{H}_2\text{O}$
3. Aluminium is industrially prepared by: [AIEEE-2002]  
(1) Fused cryolite (2) Bauxite ore (3) Alunite (4) Borax
4. For making good quality mirrors, plates of float glass are used. These are obtained by floating molten glass over a liquid metal which does not solidify before glass. The metal used can be : [AIEEE-2003]  
(1) Sodium (2) Magnesium (3) Mercury (4) Tin
5. What may be expected when phosphine gas is mixed with chlorine gas: [AIEEE-2003]  
(1)  $\text{PCl}_5$  and  $\text{HCl}$  are formed and mixture cools down  
(2)  $\text{PH}_3\cdot\text{Cl}_2$  is formed with warming up  
(3) The mixture only cools down  
(4)  $\text{PCl}_3$  and  $\text{HCl}$  are formed and the mixture warms up
6. Graphite is a soft solid lubricant extremely difficult to melt. The reason for this anomalous behaviour is that graphite : [AIEEE-2003]  
(1) Has molecules of variable molecular masses like polymers  
(2) Has carbon atoms arranged in large plates of rings of strongly bonded carbon atoms with weak interplate bonds  
(3) Is a non crystalline substance  
(4) Is an allotropic form of diamond
7. Concentrated hydrochloric acid when kept in open air sometimes produces a cloud of white fumes. This is due to : [AIEEE-2003]  
(1) Strong affinity of  $\text{HCl}$  gas for moisture in air results in forming of droplets of liquid solution which appears like a cloudy smoke  
(2) Due to strong affinity for water, conc.  $\text{HCl}$  pulls moisture of air towards self. The moisture forms droplets of water and hence the cloud  
(3) Conc.  $\text{HCl}$  emits strongly smelling  $\text{HCl}$  gas all the time  
(4) Oxygen in air reacts with emitted  $\text{HCl}$  gas to form a cloud of  $\text{Cl}_2$  gas

8. Aluminium chloride exists as dimer,  $\text{Al}_2\text{Cl}_6$  in solid state as well as in solution of non-polar solvents such as benzene. When dissolved in water, it gives- [AIEEE-2004]
- (1)  $\text{Al}^{3+} + 3\text{Cl}^-$  (2)  $[\text{Al}(\text{H}_2\text{O})_6]^{3+} + 3\text{Cl}^-$   
(3)  $[\text{Al}(\text{OH})_6]^{3-} + 3\text{HCl}$  (4)  $\text{Al}_2\text{O}_3 + 6\text{HCl}$
9. The soldiers of Napoleon army while at Alps during freezing winter suffered a serious problem as regards to the tin buttons of their uniforms. White Metallic tin buttons get converted to grey powder. This transformation is related to:- [AIEEE-2004]
- (1) An interaction with water vapour contained in humid air  
(2) A change in crystalline structure of tin  
(3) A change in the partial pressure of  $\text{O}_2$  in air  
(4) An interaction with  $\text{N}_2$  of air at low temperature
10. Which one of the following statements regarding helium is incorrect [AIEEE-2004]
- (1) It is used to produce and sustain powerful superconducting magnets  
(2) It is used as a cryogenic agent for carrying out experiments at low temperatures  
(3) It is used to fill gas balloons instead of hydrogen because it is lighter than hydrogen and non-inflammable  
(4) It is used in gas-cooled nuclear reactors
11. The number of hydrogen atoms attached to phosphorus atom in hypophosphorous acid is : [AIEEE-2005]
- (1) Zero (2) Two (3) One (4) Three
12. Heating an aqueous solution of aluminium chloride to dryness will give :- [AIEEE-2005]
- (1)  $\text{AlCl}_3$  (2)  $\text{Al}_2\text{Cl}_6$  (3)  $\text{Al}_2\text{O}_3$  (4)  $\text{Al}(\text{OH})\text{Cl}_2$
13. Which one of the following is the correct statement [AIEEE-2005]
- (1) Boric acid is a protonic acid  
(2) Beryllium exhibits coordination number of six  
(3) Chlorides of both beryllium and aluminium have bridged chloride structures in solid phase  
(4)  $\text{B}_2\text{H}_6 \cdot 2\text{NH}_3$  is known as "inorganic benzene"
14. In silicon dioxide : [AIEEE-2005]
- (1) Each silicon atom is surrounded by four oxygen atoms and each oxygen atom is bonded to two silicon atoms  
(2) Each silicon atom is surrounded by two oxygen atoms and each oxygen atom is bonded to two silicon atoms  
(3) Silicon atom is bonded to two oxygen atoms  
(4) There are double bonds between silicon and oxygen atoms

15. Regular use of which of the following fertilizer increases the acidity of soil : [AIEEE-2007]  
 (1) Potassium nitrate (2) Urea  
 (3) Superphosphate of lime (4) Ammonium sulphate
16. The stability of dihalides of Si, Ge, Sn and Pb increases steadily in the sequence: [AIEEE-2007]  
 (1)  $\text{GeX}_2 \ll \text{SiX}_2 \ll \text{SnX}_2 \ll \text{PbX}_2$  (2)  $\text{SiX}_2 \ll \text{GeX}_2 \ll \text{PbX}_2 \ll \text{SnX}_2$   
 (3)  $\text{SiX}_2 \ll \text{GeX}_2 \ll \text{SnX}_2 \ll \text{PbX}_2$  (4)  $\text{PbX}_2 \ll \text{SnX}_2 \ll \text{GeX}_2 \ll \text{SiX}_2$
17. Among the following substituted silanes the one which will give rise to cross linked silicone polymer on hydrolysis is [AIEEE-2008]  
 (1)  $\text{R}_4\text{Si}$  (2)  $\text{RSiCl}_3$  (3)  $\text{R}_2\text{SiCl}_2$  (4)  $\text{R}_3\text{SiCl}$
18. Which one of the following reactions of Xenon compounds is not feasible ? [AIEEE-2009]  
 (1)  $2\text{XeF}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Xe} + 4\text{HF} + \text{O}_2$  (2)  $\text{XeF}_6 + \text{RbF} \rightarrow \text{Rb}[\text{XeF}_7]$   
 (3)  $\text{XeO}_3 + 6\text{HF} \rightarrow \text{XeF}_6 + 3\text{H}_2\text{O}$  (4)  $3\text{XeF}_4 + 6\text{H}_2\text{O} \rightarrow 2\text{Xe} + \text{XeO}_3 + 12\text{HF} + 1.5\text{O}_2$
19. Which of the following statement is wrong ? [AIEEE-2011]  
 (1) Single N–N bond is weaker than the single P–P bond  
 (2)  $\text{N}_2\text{O}_4$  has two resonance structures  
 (3) The stability of hydrides increases from  $\text{NH}_3$  to  $\text{BiH}_3$  in group 15 of the periodic table  
 (4) Nitrogen cannot form  $d\pi\text{-p}\pi$  bond
20. Which of the following statements regarding sulphur is incorrect ? [AIEEE-2011]  
 (1) At  $600^\circ\text{C}$  the gas mainly consists of  $\text{S}_2$  molecules  
 (2) The oxidation state of sulphur is never less than +4 in its compounds  
 (3)  $\text{S}_2$  molecule is paramagnetic  
 (4) The vapour at  $200^\circ\text{C}$  consists mostly of  $\text{S}_8$  rings
21. Boron cannot form which one of the following anions ? [AIEEE-2011]  
 (1)  $\text{B}(\text{OH})_4^-$  (2)  $\text{BO}_2^-$  (3)  $\text{BF}_6^{3-}$  (4)  $\text{BH}_4^-$
22. In view of the signs of  $\Delta_r G^\circ$  for the following reactions  
 $\text{PbO}_2 + \text{Pb} \rightarrow 2 \text{PbO}, \Delta_r G^\circ < 0$   
 $\text{SnO}_2 + \text{Sn} \rightarrow 2 \text{SnO}, \Delta_r G^\circ > 0,$   
 Which oxidation states are more characteristic for lead and tin ? [AIEEE-2011]  
 (1) For lead + 4, for tin + 2 (2) For lead + 2, for tin + 2  
 (3) For lead + 4, for tin + 4 (4) For lead + 2, for tin + 4
23. The number of S–S bonds in  $\text{SO}_3$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{S}_2\text{O}_6^{2-}$  and  $\text{S}_2\text{O}_8^{2-}$  respectively are :- [Jee Main(Online)-2012]  
 (1) 1, 0, 1, 0 (2) 0, 1, 1, 0 (3) 1, 0, 0, 1 (4) 0, 1, 0, 1
24. Which one of the following depletes ozone layer ? [Jee Main(Online)-2012]  
 (1) NO and freons (2)  $\text{SO}_2$  (3) CO (4)  $\text{CO}_2$

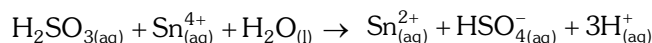
25. In which of the following arrangements, the sequence is not strictly according to the property written against it ? [Jee Main(Online)-2012]
- (1)  $\text{CO}_2 < \text{SiO}_2 < \text{SnO}_2 < \text{PbO}_2$  : increasing oxidising power
  - (2)  $\text{B} < \text{C} < \text{O} < \text{N}$  : increasing first ionisation enthalpy
  - (3)  $\text{NH}_3 < \text{PH}_3 < \text{AsH}_3 < \text{SbH}_3$  : increasing basic strength
  - (4)  $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$  : increasing acid strength
26. The formation of molecular complex  $\text{BF}_3 - \text{NH}_3$  results in a change in hybridisation of boron :-
- (1) from  $\text{sp}^3$  to  $\text{sp}^3\text{d}$
  - (2) from  $\text{sp}^2$  to  $\text{dsp}^2$  [JEE(Main) Online-2012]
  - (3) from  $\text{sp}^3$  to  $\text{sp}^2$
  - (4) from  $\text{sp}^2$  to  $\text{sp}^3$
27. The catenation tendency of C, Si and Ge is in the order  $\text{Ge} < \text{Si} < \text{C}$ . The bond energies (in  $\text{kJ mol}^{-1}$ ) of C—C, Si—Si and Ge—Ge bonds are respectively : [JEE(Main) Online-2013]
- (1) 348, 260, 297
  - (2) 348, 297, 260
  - (3) 297, 348, 260
  - (4) 260, 297, 348
28. The gas evolved on heating  $\text{CaF}_2$  and  $\text{SiO}_2$  with concentrated  $\text{H}_2\text{SO}_4$ , on hydrolysis gives a white gelatinous precipitate. The precipitate is: [Jee Main(Online)-2014]
- (1) silica gel
  - (2) silicic acid
  - (3) hydrofluosilicic acid
  - (4) calciumfluorosilicate
29. Which of the following series correctly represents relations between the elements from X to Y?
- |                                                     |                                                     |                         |
|-----------------------------------------------------|-----------------------------------------------------|-------------------------|
|                                                     | $\text{X} \rightarrow \text{Y}$                     | [Jee Main(Online)-2014] |
| (1) ${}_{18}\text{Ar} \rightarrow {}_{54}\text{Xe}$ | Noble character increases                           |                         |
| (2) ${}_3\text{Li} \rightarrow {}_{19}\text{K}$     | Ionization enthalpy increases                       |                         |
| (3) ${}_6\text{C} \rightarrow {}_{32}\text{Ge}$     | Atomic radii increases                              |                         |
| (4) ${}_9\text{F} \rightarrow {}_{35}\text{Br}$     | Electron gain enthalpy with negative sign increases |                         |
30. Which of the following statements about the depletion of ozone layer is correct? [Jee Main(Online)-2014]
- (1) The problem of ozone depletion is more serious at poles because ice crystals in the clouds over poles act as catalyst for photochemical reactions involving the decomposition of ozone by  $\text{Cl}^\bullet$  and  $\text{ClO}^\bullet$  radicals
  - (2) The problem of ozone depletion is less serious at poles because  $\text{NO}_2$  solidifies and is not available for consuming  $\text{ClO}^\bullet$  radicals
  - (3) Oxides of nitrogen also do not react with ozone in stratosphere
  - (4) Freons, chlorofluorocarbons, are inert chemically, they do not react with ozone in stratosphere
31. Which of the following xenon-OXO compounds may not be obtained by hydrolysis of xenon fluorides ? [Jee Main(Online)-2014]
- (1)  $\text{XeO}_2\text{F}_2$
  - (2)  $\text{XeO}_3$
  - (3)  $\text{XeO}_4$
  - (4)  $\text{XeOF}_4$



32. Hydrogen peroxide acts both as an oxidising and as a reducing agent depending upon the nature of the reacting species. In which of the following cases  $\text{H}_2\text{O}_2$  acts as a reducing agent in acid medium ? [Jee Main(Online)-2014]

(1)  $\text{MnO}_4^-$  (2)  $\text{SO}_3^{2-}$  (3) KI (4)  $\text{Cr}_2\text{O}_7^{2-}$

33. Consider the reaction [Jee Main(Online)-2014]



Which of the following statements is correct?

- (1)  $\text{H}_2\text{SO}_3$  is the reducing agent because it undergoes oxidation  
 (2)  $\text{H}_2\text{SO}_3$  is the reducing agent because it undergoes reduction  
 (3)  $\text{Sn}^{4+}$  is the reducing agent because it undergoes oxidation  
 (4)  $\text{Sn}^{4+}$  is the oxidizing agent because it undergoes oxidation
34. In the following sets of reactants which two sets best exhibit the amphoteric character of  $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$  ? [JEE(Main) Online-2014]

Set-1 :  $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}(\text{s})$  and  $\text{OH}^- (\text{aq})$

Set-2 :  $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}(\text{s})$  and  $\text{H}_2\text{O} (\ell)$

Set-3 :  $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}(\text{s})$  and  $\text{H}^+ (\text{aq})$

Set-4 :  $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}(\text{s})$  and  $\text{NH}_3 (\text{aq})$

(1) 1 and 2 (2) 2 and 4 (3) 1 and 3 (4) 3 and 4

35. Which of the following compounds has a P-P bond :- [Jee Main(Online)-2015]

(1)  $\text{H}_4\text{P}_2\text{O}_5$  (2)  $(\text{HPO}_3)_3$  (3)  $\text{H}_4\text{P}_2\text{O}_7$  (4)  $\text{H}_4\text{P}_2\text{O}_6$

36. Chlorine water on standing loses its colour and forms :- [Jee Main(Online)-2015]

(1) HCl and  $\text{HClO}_2$  (2) HCl only  
 (3)  $\text{HOCl}$  and  $\text{HOCl}_2$  (4) HCl and  $\text{HOCl}$

37. Which among the following is the most reactive ? [Jee Main-2015]

(1)  $\text{I}_2$  (2)  $\text{ICl}$  (3)  $\text{Cl}_2$  (4)  $\text{Br}_2$

38. Which one has the highest boiling point ? [Jee Main-2015]

(1) Kr (2) Xe (3) He (4) Ne

39. From the following statements regarding  $\text{H}_2\text{O}_2$ , choose the incorrect statement : [Jee Main-2015]

(1) It has to be stored in plastic or wax lined glass bottles in dark  
 (2) It has to be kept away from dust  
 (3) It can act only as an oxidizing agent  
 (4) It decomposes on exposure to light

40. The reaction of zinc with dilute and concentrated nitric acid, respectively produces :

[JEE (Main) 2016]

- (1)  $\text{NO}_2$  and  $\text{N}_2\text{O}$       (2)  $\text{N}_2\text{O}$  and  $\text{NO}_2$       (3)  $\text{NO}_2$  and  $\text{NO}$       (4)  $\text{NO}$  and  $\text{N}_2\text{O}$

41. The non-metal that does not exhibit positive oxidation state is :

[JEE (Main) 2016]

- (1) Oxygen      (2) Fluorine      (3) Iodine      (4) Chlorine

42. Which intermolecular force is most responsible in allowing xenon gas to liquefy?

[JEE (Main) Online 2016]

- (1) Ionic      (2) Instantaneous dipole- induced dipole  
(3) Dipole - dipole      (4) Ion - dipole

43. The following statements concern elements in the periodic table. Which of the following is true ?

[JEE (Main) Online 2016]

- (1) The group 13 elements are all metals.  
(2) For group 15 elements, the stability of +5 oxidation state increases down the group.  
(3) All the elements in Group 17 are gases.  
(4) Elements of group 16 have lower ionization enthalpy values compared to those of group 15 in the corresponding periods.

44. **Assertion :** Among the carbon allotropes, diamond is an insulator, whereas, graphite is a good conductor of electricity.

[JEE (Main) Online 2016]

**Reason :** Hybridization of carbon in diamond and graphite are  $\text{sp}^3$  and  $\text{sp}^2$ , respectively.

- (1) Assertion is incorrect statement, but the reason is correct.  
(2) Both assertion and reason are correct, and the reason is the correct explanation for the assertion.  
(3) Both assertion and reason are incorrect.  
(4) Both assertion and reason are correct, but the reason is not the correct explanation for the assertion.

45. Identify the incorrect statement :

[JEE (Main) Online 2016]

- (1)  $\text{S}_8$  ring has a crown shape.  
(2) The S-S-S bond angles in the  $\text{S}_8$  and  $\text{S}_6$  rings are the same  
(3)  $\text{S}_2$  is paramagnetic like oxygen  
(4) Rhombic and monoclinic sulphur have  $\text{S}_8$  molecules.

46. Which of the following reactions is an example of a redox reaction ?

[JEE (Main) 2017]

- (1)  $\text{XeF}_4 + \text{O}_2\text{F}_2 \rightarrow \text{XeF}_6 + \text{O}_2$   
(2)  $\text{XeF}_2 + \text{PF}_5 \rightarrow [\text{XeF}]^+ \text{PF}_6^-$   
(3)  $\text{XeF}_6 + \text{H}_2\text{O} \rightarrow \text{XeOF}_4 + 2\text{HF}$   
(4)  $\text{XeF}_6 + 2\text{H}_2\text{O} \rightarrow \text{XeO}_2\text{F}_2 + 4\text{HF}$

47. The products obtained when chlorine gas reacts with cold and dilute aqueous NaOH are :-

- (1)  $\text{ClO}^-$  and  $\text{ClO}_3^-$       (2)  $\text{ClO}_2^-$  and  $\text{ClO}_3^-$   
(3)  $\text{Cl}^-$  and  $\text{ClO}^-$       (4)  $\text{Cl}^-$  and  $\text{ClO}_2^-$

[JEE (Main) 2017]

48. In which of the following reaction, hydrogen peroxide acts as an oxidizing agent ?  
 (1)  $I_2 + H_2O_2 + 2OH^- \rightarrow 2I^- + 2H_2O + O_2$  [JEE (Main) ONLINE 2017]  
 (2)  $HOCl + H_2O_2 \rightarrow H_3O^+ + Cl^- + O_2$   
 (3)  $PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O$   
 (4)  $2MnO_4^- + 3H_2O_2 \rightarrow 2MnO_2 + 3O_2 + 2H_2O + 2OH^-$
49.  $XeF_6$  on partial hydrolysis with water produces a compound 'X'. The same compound 'X' is formed when  $XeF_6$  reacts with silica. The compound 'X' is:- [JEE (Main) ONLINE 2017]  
 (1)  $XeO_3$  (2)  $XeF_4$  (3)  $XeOF_4$  (4)  $XeF_2$
50. The compound that does not produce nitrogen gas by the thermal decomposition is [JEE (Main) OFFLINE 2018]  
 (1)  $(NH_4)_2Cr_2O_7$  (2)  $NH_4NO_2$  (3)  $(NH_4)_2SO_4$  (4)  $Ba(N_3)_2$
51. For per gram of reactant, the maximum quantity of  $N_2$  gas is produced in which of the following thermal decomposition reactions ? [JEE (Main) ONLINE 2018]  
 (Given : Atomic wt. – Cr = 52u, Ba = 137u)  
 (1)  $2NH_4NO_3(s) \rightarrow 2N_2(g) + 4H_2O(g) + O_2(g)$   
 (2)  $Ba(N_3)_2(s) \rightarrow Ba(s) + 3N_2(g)$   
 (3)  $(NH_4)_2Cr_2O_7(s) \rightarrow N_2(g) + 4H_2O(g)$   
 (4)  $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$
52. Lithium aluminium hydride reacts with silicon tetrachloride to form :- [JEE (Main) ONLINE 2018]  
 (1)  $LiCl$ ,  $AlCl_3$  and  $SiH_4$  (2)  $LiCl$ ,  $AlH_3$  and  $SiH_4$   
 (3)  $LiH$ ,  $AlCl_3$  and  $SiCl_2$  (4)  $LiH$ ,  $AlH_3$  and  $SiH_4$
53. Xenon hexafluoride on partial hydrolysis produces compounds 'X' and 'Y' Compounds 'X' and 'Y' and the oxidation state of Xe are respectively : [JEE (Main) ONLINE 2018]  
 (1)  $XeO_2F_2(+6)$  and  $XeO_2(+4)$  (2)  $XeOF_4(+6)$  and  $XeO_2F_2(+6)$   
 (3)  $XeOF_4(+6)$  and  $XeO_3(+6)$  (4)  $XeO_2(+4)$  and  $XeO_3(+6)$
54. Which of the following is a lewis acid ? [JEE (Main) ONLINE 2018]  
 (1)  $NaH$  (2)  $NF_3$  (3)  $PH_3$  (4)  $B(CH_3)_3$

## EXERCISE # J-ADVANCED

## (IIT JEE ASKED QUESTIONS)

## Fill in the blanks

- Give reason : [IIT- 2000]  
Why elemental nitrogen exists as a diatomic molecule whereas elemental phosphorus is a tetra atomic molecule.
- Give an example of oxidation of one halide by another halogen. Explain the feasibility of the reaction. [IIT- 2000]
- Compounds X on reduction with  $\text{LiAlH}_4$  gives a hydride Y containing 21.72% hydrogen alongwith other products. The compound Y reacts with air explosively resulting in boron trioxide. Identify X and Y. Give balanced reactions involved in the formation of Y and its reaction with air Draw the structure of Y. [IIT- 2001]
- Starting from  $\text{SiCl}_4$ , prepare the following in steps not exceeding the number given in parenthesis (reactions only) [IIT- 2001]
  - Silicon (1)
  - Linear silicon containing methyl group only (4)
  - $\text{Na}_2\text{SiO}_3$  (3)
- Write the balanced chemical equation for developing photographic films. [IIT- 2001]
- Identify (X) in the following synthetic scheme and write their structures. [IIT- 2001]  
 $\text{BaCO}_3^* + \text{H}_2\text{SO}_4 \longrightarrow \text{X (gas)}$  (C denotes  $\text{C}^{14}$ )
- Write the balanced equations for the reactions of the following compounds with water [IIT-2002]
 

|                              |                     |                     |                     |                    |
|------------------------------|---------------------|---------------------|---------------------|--------------------|
| (i) $\text{Al}_4\text{Cl}_3$ | (ii) $\text{CaNCN}$ | (iii) $\text{BF}_3$ | (iv) $\text{NCl}_3$ | (v) $\text{XeF}_3$ |
|------------------------------|---------------------|---------------------|---------------------|--------------------|
- Write the balanced equations for the reactions of the following compounds with water: [IIT- 2002]
 

|                             |                     |                     |                     |                    |
|-----------------------------|---------------------|---------------------|---------------------|--------------------|
| (i) $\text{Al}_4\text{C}_3$ | (ii) $\text{CaNCN}$ | (iii) $\text{BF}_3$ | (iv) $\text{NCl}_3$ | (v) $\text{XeF}_4$ |
|-----------------------------|---------------------|---------------------|---------------------|--------------------|
- Identify the following:  

$$\text{Na}_2\text{CO}_3 \xrightarrow[\text{(aq)}]{\text{SO}_2} \text{A} \xrightarrow{\text{Na}_2\text{CO}_3} \text{B} \xrightarrow[\Delta]{\text{elemental S}} \text{C} \xrightarrow{\text{I}_2} \text{D}$$
 [IIT- 2003]  
 Also mention the oxidation state of S in all the compounds.
- Arrange the following oxides in the increasing order of Bronsted basicity. [IIT- 2004]  
 $\text{Cl}_2\text{O}_7$ ,  $\text{BaO}$ ,  $\text{SO}_3$ ,  $\text{CO}_2$ ,  $\text{B}_2\text{O}_3$
- The number of P—O—P bonds in cyclic tetrametaphosphoric acid is – [IIT-2000]
 

|          |         |           |          |
|----------|---------|-----------|----------|
| (A) Zero | (B) Two | (C) Three | (D) Four |
|----------|---------|-----------|----------|
- The correct order of acidic strength is – [IIT- 2000]
 

|                                                                     |                                                        |
|---------------------------------------------------------------------|--------------------------------------------------------|
| (A) $\text{Cl}_2\text{O}_7 > \text{SO}_2 > \text{P}_4\text{O}_{10}$ | (B) $\text{CO}_2 > \text{N}_2\text{O}_5 > \text{SO}_3$ |
| (C) $\text{Na}_2\text{O} > \text{MgO} > \text{Al}_2\text{O}_3$      | (D) $\text{K}_2\text{O} > \text{CaO} > \text{MgO}$     |

13. Amongst  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{Se}$  and  $\text{H}_2\text{Te}$ , the one with the highest boiling point is – [IIT- 2000]  
 (A)  $\text{H}_2\text{O}$  because of hydrogen bonding (B)  $\text{H}_2\text{Te}$  because of higher molecular weight  
 (C)  $\text{H}_2\text{S}$  because of hydrogen bonding (D)  $\text{H}_2\text{Se}$  because of lower molecular weight.
14. Ammonia can be dried by – [IIT- 2000]  
 (A) Conc.  $\text{H}_2\text{SO}_4$  (B)  $\text{P}_4\text{O}_{10}$  (C)  $\text{CaO}$  (D) Anhydrous  $\text{CaCl}_2$
15. Which of the following are hydrolysed – [REE 2000]  
 (A)  $\text{NCl}_3$  (B)  $\text{BCl}_3$  (C)  $\text{CCl}_4$  (D)  $\text{SiCl}_4$
16. The set with correct order of acidity is – [IIT- 2001]  
 (A)  $\text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$   
 (B)  $\text{HClO}_4 < \text{HClO}_3 < \text{HClO}_2 < \text{HClO}$   
 (C)  $\text{HClO} < \text{HClO}_4 < \text{HClO}_3 < \text{HClO}_2$   
 (D)  $\text{HClO}_4 < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}$
17. The reaction,  $3\text{ClO}^- (\text{aq}) \longrightarrow \text{ClO}_3^- (\text{aq}) + 2\text{Cl}^- (\text{aq})$  is an example of – [IIT- 2001]  
 (A) Oxidation reaction (B) reduction reaction  
 (C) Disproportionation reaction (D) Decomposition reaction
18. The number of S–S bonds in sulphur trioxide trimer,  $(\text{S}_3\text{O}_9)$  is – [IIT- 2001]  
 (A) Three (B) Two (C) One (D) Zero
19. **Statement-I :** Between  $\text{SiCl}_4$  and  $\text{CCl}_4$ , only  $\text{SiCl}_4$  reacts with water [IIT- 2001]  
**Because :**  
**Statement-II :**  $\text{SiCl}_4$  is ionic and  $\text{CCl}_4$  is covalent  
 (A) If both assertion and reason are correct and reason is the correct explanation of the assertion  
 (B) If both assertion and reason are correct, but reason is not the correct explanation of the assertion  
 (C) If assertion is correct, but reason is incorrect  
 (D) If assertion is incorrect, but reason is correct.
20. Polyphosphates are used as water softening agents because they – [IIT- 2002]  
 (A) Form soluble complexes with anionic species  
 (B) Precipitate anionic species  
 (C) Form soluble complexes with cationic species  
 (D) Precipitate cationic species
21. Identify the correct order of solubility of  $\text{Na}_2\text{S}$ ,  $\text{CuS}$ , and  $\text{ZnS}$  in aqueous medium – [IIT- 2002]  
 (A)  $\text{CuS} > \text{ZnS} > \text{Na}_2\text{S}$  (B)  $\text{ZnS} > \text{Na}_2\text{S} > \text{CuS}$   
 (C)  $\text{Na}_2\text{S} > \text{CuS} > \text{ZnS}$  (D)  $\text{Na}_2\text{S} > \text{ZnS} > \text{CuS}$
22. Identify, the correct order of acidic strength of  $\text{CO}_2$ ,  $\text{CuO}$ ,  $\text{CaO}$ ,  $\text{H}_2\text{O}$  – [IIT- 2002]  
 (A)  $\text{CaO} < \text{CuO} < \text{H}_2\text{O} < \text{CO}_2$  (B)  $\text{H}_2\text{O} < \text{CuO} < \text{CaO} < \text{CO}_2$   
 (C)  $\text{CaO} < \text{H}_2\text{O} < \text{CuO} < \text{CO}_2$  (D)  $\text{H}_2\text{O} < \text{CO}_2 < \text{CaO} < \text{CuO}$

23.  $\text{H}_3\text{BO}_3$  is – [IIT- 2002, 3]  
 (A) Monobasic acid and weak Lewis acid (B) Monobasic and weak Bronsted acid  
 (C) Monobasic and strong Lewis acid (D) Tribasic and weak Bronsted acid
24. When  $\text{I}^-$  is oxidised by  $\text{MnO}_4^-$  in alkaline medium,  $\text{I}^-$  converts into – [IIT- 2003]  
 (A)  $\text{IO}_3^-$  (B)  $\text{I}_2$  (C)  $\text{IO}_4^-$  (D)  $\text{IO}^-$
25. **Column-I (Change)** **Column-II (Given change is done by)**  
 (A)  $\text{Bi}^{3+} \longrightarrow (\text{BiO})^+$  (p) Heat [IIT- 2003]  
 (B)  $[\text{AlO}_2]^- \longrightarrow \text{Al}(\text{OH})_3$  (q) Hydrolysis  
 (C)  $\text{SiO}_4^{4-} \longrightarrow \text{Si}_2\text{O}_7^{6-}$  (r) Acidification  
 (D)  $(\text{B}_4\text{O}_7^{2-}) \longrightarrow [\text{B}(\text{OH})_3]$  (s) Dilution by water
26.  $(\text{Me})_2\text{SiCl}_2$  on hydrolysis will produce – [IIT- 2003]  
 (A)  $(\text{Me})_2\text{Si}(\text{OH})_2$  (B)  $(\text{Me})_2\text{Si}=\text{O}$   
 (C)  $[-(\text{Me})_2\text{Si}-\text{O}-]_n$  (D)  $\text{Me}_2\text{SiCl}(\text{OH})$
27. Which is the most thermodynamically stable allotropic form of phosphorus? [IIT- 2004]  
 (A) Red (B) White (C) Black (D) Yellow
28. When  $\text{PbO}_2$  reacts with conc.  $\text{HNO}_3$  the gas evolved may be : [2005]  
 (A)  $\text{NO}_2$  (B)  $\text{O}_2$  (C)  $\text{N}_2$  (D)  $\text{N}_2\text{O}$
29. Which of the following is not oxidised by  $\text{O}_3$ ? [IIT- 2005]  
 (A) KI (B)  $\text{FeSO}_4$  (C)  $\text{KMnO}_4$  (D)  $\text{K}_2\text{MnO}_4$
30. Which blue-liquid is obtained on reacting equimolar amounts of two gases at  $-30^\circ\text{C}$ ? [IIT- 2005]  
 (A)  $\text{N}_2\text{O}$  (B)  $\text{N}_2\text{O}_3$  (C)  $\text{N}_2\text{O}_4$  (D)  $\text{N}_2\text{O}_5$
31.  $\text{B}(\text{OH})_3 + \text{NaOH} \rightleftharpoons \text{NaBO}_2 + \text{Na}[\text{B}(\text{OH})_4] + \text{H}_2\text{O}$  how can this reaction is made to proceed in forward direction? [IIT- 2006]  
 (A) Addition of cis 1, 2 diol (B) Addition of borax  
 (C) Addition of trans 1, 2 diol (D) Addition of  $\text{Na}_2\text{HPO}_4$
32. Among the following, the paramagnetic compound is – [IIT- 2007]  
 (A)  $\text{Na}_2\text{O}_2$  (B)  $\text{O}_3$  (C)  $\text{N}_2\text{O}$  (D)  $\text{KO}_2$
33. **Statement-I** : Boron always forms covalent bond [2007]  
**Because :**  
**Statement-II** : The small size of  $\text{B}^{3+}$  favours formation of covalent bond.  
 (A) Statement-I is True, Statement-II is True, Statement-II is a correct explanation for Statement-I  
 (B) Statement-I is True, Statement-II is True, Statement-II is not a correct explanation for Statement-II  
 (C) Statement-I is True, Statement-II is False  
 (D) Statement-I is False, Statement-II is True

34. **Statement-I** : In water, orthoboric acid behaves as a weak monobasic acid. [2007]

**Statement-II** : In water, orthoboric acid acts as a proton donor.

- (A) Statement-I is True, Statement-II is True, Statement-II is a correct explanation for Statement-I  
(B) Statement-I is True, Statement-II is True, Statement-II is not a correct explanation for Statement-II  
(C) Statement-I is True, Statement-II is False  
(D) Statement-I is False, Statement-II is True

**Comprehension # 1 (Q. 35 to 37)**

The noble gases have closed-shell electronic configuration and are monoatomic gases under normal conditions. The low boiling point of the lighter noble gases are due to weak dispersion forces between the atoms and the absence of other interatomic interactions. The direct reaction of xenon with fluorine leads to a series of compounds with oxidation number + 2, + 4 and + 6.  $\text{XeF}_4$  reacts violently with water to give  $\text{XeO}_3$ . The compounds of xenon exhibit rich stereochemistry and their geometries can be deduced considering the total number of electron pairs in the valence shell. [IIT- 2007]

35. Argon is used in arc welding because of its –

- (A) Low reactivity with metal (B) Ability to lower the melting point of metal  
(C) Flammability (D) High calorific value

36. The structure of  $\text{XeO}_3$  is –

- (A) Linear (B) Planar (C) Pyramidal (D) T-shaped

37.  $\text{XeF}_4$  and  $\text{XeF}_6$  are expected to be –

- (A) Oxidising agent (B) Reducing agent (C) Unreactive (D) Strongly basic

**Comprehension # 2 (Q.38 to 40)**

There are some deposits of nitrates and phosphates in earth's crust. Nitrates are more soluble in water. Nitrates are difficult to reduce under the laboratory conditions but microbes do it easily. Ammonia forms large number of complexes with transition metal ions. Hybridization easily explains the ease of sigma donation capability of  $\text{NH}_3$  and  $\text{PH}_3$ . Phosphine is a flammable gas and is prepared from white phosphorous. IIT- 2008]

38. Among the following, the correct statement is :-

- (A) Phosphates have no biological significance in humans  
(B) Between nitrates and phosphates, phosphates are less abundant in earth's crust  
(C) Between nitrates and phosphates, nitrates are less abundant in earth's crust  
(D) Oxidation of nitrates is possible in soil

39. Among the following, the correct statement is :-

- (A) Between  $\text{NH}_3$  and  $\text{PH}_3$ ,  $\text{NH}_3$  is a better electron donor because the lone pair of electrons occupies spherical 's' orbital and is less directional  
(B) Between  $\text{NH}_3$  and  $\text{PH}_3$ ,  $\text{PH}_3$  is a better electron donor because the lone pair of electrons occupies  $\text{sp}^3$  orbital and is more directional  
(C) Between  $\text{NH}_3$  and  $\text{PH}_3$ ,  $\text{NH}_3$  is a better electron donor because the lone pair of electrons occupies  $\text{sp}^3$  orbital and is more directional  
(D) Between  $\text{NH}_3$  and  $\text{PH}_3$ ,  $\text{PH}_3$  is a better electron donor because the lone pair of electrons occupies spherical 's' orbital and is less directional.

40. White phosphorus on reaction with NaOH gives  $\text{PH}_3$  as one of the products. This is a :-  
 (A) dimerization reaction (B) disproportionation reaction  
 (C) condensation reaction (D) precipitation reaction
41. The reaction of  $\text{P}_4$  with X leads selectively to  $\text{P}_4\text{O}_6$ . The X is [JEE 2009]  
 (A) Dry  $\text{O}_2$  (B) A mixture of  $\text{O}_2$  and  $\text{N}_2$   
 (C) Moist  $\text{O}_2$  (D)  $\text{O}_2$  in the presence of aqueous NaOH
42. The reaction of white phosphorus with aqueous NaOH gives phosphine along with another phosphorus containing compound. The reaction type ; the oxidation states of phosphorus in phosphine and the other product are respectively [JEE 2012]  
 (A) redox reaction ; -3 and -5 (B) redox reaction ; +3 and +5  
 (C) disproportionation reaction ; -3 and +1 (D) disproportionation reaction ; -3 and +3
43. Bleaching powder contains a salt of an oxoacid as one of its components. The anhydride of that oxoacid is :  
 (A)  $\text{Cl}_2\text{O}$  (B)  $\text{Cl}_2\text{O}_7$  (C)  $\text{ClO}_2$  (D)  $\text{Cl}_2\text{O}_6$  [JEE 2012]
44. With respect to graphite and diamond, which of the statement(s) given below is (are) correct ? [JEE 2012]  
 (A) Graphite is harder than diamond.  
 (B) Graphite has higher electrical conductivity than diamond.  
 (C) Graphite has higher thermal conductivity than diamond.  
 (D) Graphite has higher C-C bond order than diamond.
45. Concentrated nitric acid, upon long standing, turns yellow-brown due to the formation of -  
 (A) NO (B)  $\text{NO}_2$  (C)  $\text{N}_2\text{O}$  (D)  $\text{N}_2\text{O}_4$  [JEE 2013]
46. The correct statement(s) about  $\text{O}_3$  is(are) [JEE 2013]  
 (A) O-O bond lengths are equal (B) Thermal decomposition of  $\text{O}_3$  is endothermic  
 (C)  $\text{O}_3$  is diamagnetic in nature (D)  $\text{O}_3$  has a bent structure

### Comprehension # 3 (Q. 47 and 48)

The reaction of  $\text{Cl}_2$  gas with cold dilute and hot concentrated NaOH in water give sodium salt of two (different) oxoacids of chlorine P and Q respectively. The  $\text{Cl}_2$  gas reacts with  $\text{SO}_2$  gas, in presence of charcoal to give a product R. R reacts with white phosphorous to give a compound S. On hydrolysis, S gives as oxoacid of phosphorous T.

47. R, S and T, respectively are - [JEE 2013]  
 (A)  $\text{SO}_2\text{Cl}_2$ ,  $\text{PCl}_5$  and  $\text{H}_3\text{PO}_4$  (B)  $\text{SO}_2\text{Cl}_2$ ,  $\text{PCl}_3$  and  $\text{H}_3\text{PO}_3$   
 (C)  $\text{SOCl}_2$ ,  $\text{PCl}_3$  and  $\text{H}_3\text{PO}_2$  (D)  $\text{SOCl}_2$ ,  $\text{PCl}_3$  and  $\text{H}_3\text{PO}_3$
48. P and Q, respectively, are the sodium salts of -  
 (A) Hypochlorous and chloric acid (B) Hypochlorous and chlorus acid  
 (C) Chloric and perchloric acids (D) Chloric and hypochlorous acids



49. The unbalanced chemical reactions given in List-I show missing reagent or condition (?) which are provided in List-II. Match List-I with List-II and select the correct answer using the code given below the lists : [JEE 2013]

**List-I**

- (P)  $\text{PbO}_2 + \text{H}_2\text{SO}_4 \xrightarrow{?} \text{PbSO}_4 + \text{O}_2 + \text{other product}$   
 (Q)  $\text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} \xrightarrow{?} \text{NaHSO}_4 + \text{other product}$   
 (R)  $\text{N}_2\text{H}_4 \xrightarrow{?} \text{N}_2 + \text{other product}$   
 (S)  $\text{XeF}_2 \xrightarrow{?} \text{Xe} + \text{other product}$

**List-II**

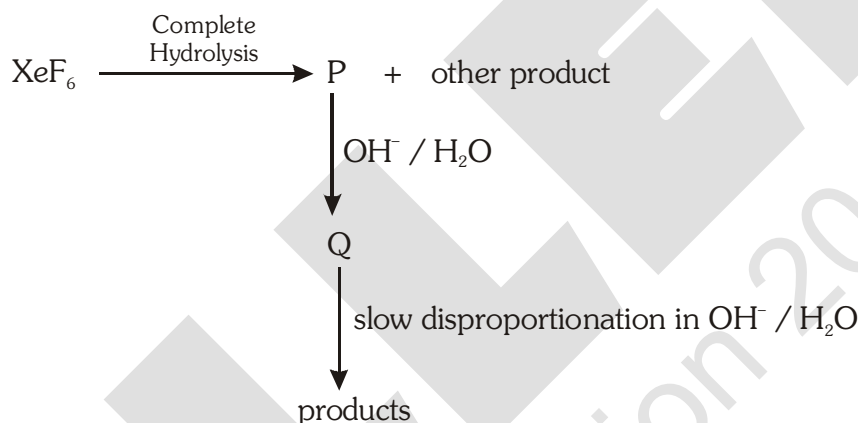
- (1) NO  
 (2)  $\text{I}_2$   
 (3) Warm  
 (4)  $\text{Cl}_2$

**Codes :**

- |     | P | Q | R | S |
|-----|---|---|---|---|
| (A) | 4 | 2 | 3 | 1 |
| (C) | 1 | 4 | 2 | 3 |

- |     | P | Q | R | S |
|-----|---|---|---|---|
| (B) | 3 | 2 | 1 | 4 |
| (D) | 3 | 4 | 2 | 1 |

50. Under ambient conditions, the total number of gases released as products in the final step of the reaction scheme shown below is [JEE Adv. 2014]



- (A) 0 (B) 1 (C) 2 (D) 3

51. The product formed in the reaction of  $\text{SOCl}_2$  with white phosphorous is [JEE Adv. 2014]

- (A)  $\text{PCl}_3$  (B)  $\text{SO}_2\text{Cl}_2$  (C)  $\text{SCl}_2$  (D)  $\text{POCl}_3$

52. The **CORRECT** statement(s) for orthoboric acid is / are - [JEE Adv. 2014]

- (A) It behaves as a weak acid in water due to self ionization  
 (B) Acidity of its aqueous solution increases upon addition of ethylene glycol  
 (C) It has a three dimensional structure due to hydrogen bonding.  
 (D) It is a weak electrolyte in water

53. The correct statement(s) regarding, (i)  $\text{HClO}$ , (ii)  $\text{HClO}_2$ , (iii)  $\text{HClO}_3$  and (iv)  $\text{HClO}_4$ , is(are) [JEE Adv. 2015]

- (A) The number of  $\text{Cl}=\text{O}$  bonds in (ii) and (iii) together is two  
 (B) The number of lone pairs of electrons on Cl in (ii) and (iii) together is three  
 (C) The hybridization of Cl in (iv) is  $\text{sp}^3$   
 (D) Amongst (i) to (iv), the strongest acid is (i)



62. The order of the oxidation state of the phosphorus atom in  $\text{H}_3\text{PO}_2$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{H}_3\text{PO}_3$  and  $\text{H}_4\text{P}_2\text{O}_6$  is [JEE Adv. 2017]

- (A)  $\text{H}_3\text{PO}_4 > \text{H}_4\text{P}_2\text{O}_6 > \text{H}_3\text{PO}_3 > \text{H}_3\text{PO}_2$   
 (B)  $\text{H}_3\text{PO}_3 > \text{H}_3\text{PO}_2 > \text{H}_3\text{PO}_4 > \text{H}_4\text{P}_2\text{O}_6$   
 (C)  $\text{H}_3\text{PO}_2 > \text{H}_3\text{PO}_3 > \text{H}_4\text{P}_2\text{O}_6 > \text{H}_3\text{PO}_4$   
 (D)  $\text{H}_3\text{PO}_4 > \text{H}_3\text{PO}_2 > \text{H}_3\text{PO}_3 > \text{H}_4\text{P}_2\text{O}_6$

63. The option(s) with only amphoteric oxides is (are): [JEE Adv. 2017]

- (A)  $\text{Cr}_2\text{O}_3$ ,  $\text{CrO}$ ,  $\text{SnO}$ ,  $\text{PbO}$   
 (B)  $\text{NO}$ ,  $\text{B}_2\text{O}_3$ ,  $\text{PbO}$ ,  $\text{SnO}_2$   
 (C)  $\text{Cr}_2\text{O}_3$ ,  $\text{BeO}$ ,  $\text{SnO}$ ,  $\text{SnO}_2$   
 (D)  $\text{ZnO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{PbO}$ ,  $\text{PbO}_2$

64. Among the following, the correct statement(s) is are [JEE Adv. 2017]

- (A)  $\text{Al}(\text{CH}_3)_3$  has the three-centre two-electron bonds in its dimeric structure  
 (B)  $\text{AlCl}_3$  has the three-centre two-electron bonds in its dimeric structure  
 (C)  $\text{BH}_3$  has the three-centre two-electron bonds in its dimeric structure  
 (D) The Lewis acidity of  $\text{BCl}_3$  is greater than that of  $\text{AlCl}_3$

#### Paragraph for Q.65 & 66

Upon heating  $\text{KClO}_3$  in the presence of catalytic amount of  $\text{MnO}_2$ , a gas **W** is formed. Excess amount of **W** reacts with white phosphorus to give **X**. The reaction of **X** with pure  $\text{HNO}_3$  gives **Y** and **Z**. [JEE Adv. 2017]

65. **W** and **X** are, respectively

- (A)  $\text{O}_3$  and  $\text{P}_4\text{O}_6$  (B)  $\text{O}_2$  and  $\text{P}_4\text{O}_{10}$  (C)  $\text{O}_3$  and  $\text{P}_4\text{O}_{10}$  (D)  $\text{O}_2$  and  $\text{P}_4\text{O}_6$

66. **Y** and **Z** are, respectively

- (A)  $\text{N}_2\text{O}_4$  and  $\text{H}_3\text{PO}_3$  (B)  $\text{N}_2\text{O}_4$  and  $\text{HPO}_3$   
 (C)  $\text{N}_2\text{O}_5$  and  $\text{HPO}_3$  (D)  $\text{N}_2\text{O}_3$  and  $\text{H}_3\text{PO}_4$

67. The compound(s) which generate(s)  $\text{N}_2$  gas upon thermal decomposition below  $300^\circ\text{C}$  is (are) [IIT JEE 2018]

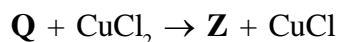
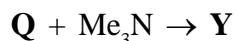
- (A)  $\text{NH}_4\text{NO}_3$  (B)  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  (C)  $\text{Ba}(\text{N}_3)_2$  (D)  $\text{Mg}_3\text{N}_2$

#### INTEGER

68. The total number of compounds having at least one bridging oxo group among the molecules given below is \_\_\_\_\_. [JEE Adv. 2018]

$\text{N}_2\text{O}_3$ ,  $\text{N}_2\text{O}_5$ ,  $\text{P}_4\text{O}_6$ ,  $\text{P}_4\text{O}_7$ ,  $\text{H}_4\text{P}_2\text{O}_5$ ,  $\text{H}_5\text{P}_3\text{O}_{10}$ ,  $\text{H}_2\text{S}_2\text{O}_3$ ,  $\text{H}_2\text{S}_2\text{O}_5$

69. A tin chloride **Q** undergoes the following reactions (not balanced) [JEE Adv. 2019]



**X** is a monoanion having pyramidal geometry. Both **Y** and **Z** are neutral compounds. Choose the correct option(s).

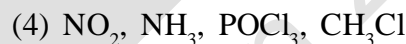
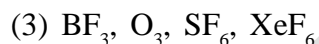
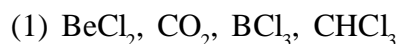
- (1) The central atoms in **X** is  $\text{sp}^3$  hybridized
- (2) The oxidation state of the central atom in **Z** is +2
- (3) The central atom in **Z** has one lone pair of electrons
- (4) There is a coordinate bond in **Y**

70. At 143 K. the reaction of  $\text{XeF}_4$  with  $\text{O}_2\text{F}_2$  produces a xenon compound **Y**. The total number of lone pair(s) of electrons present on the whole molecule of **Y** is \_\_\_\_\_ [JEE Adv. 2019]

71. The amount of water produced (in g) in the oxidation of 1 mole of rhombic sulphur by conc.  $\text{HNO}_3$  to a compound with the highest oxidation state of sulphur is \_\_\_\_ [JEE Adv. 2019]

(Given data : Molar mass of water =  $18 \text{ g mol}^{-1}$ )

72. Each of the following options contains a set of four molecules. Identify the option(s) where all four molecules possess permanent dipole moment at room temperature. [JEE Adv. 2019]



73. Among  $\text{B}_2\text{H}_6$ ,  $\text{B}_3\text{N}_3\text{H}_6$ ,  $\text{N}_2\text{O}$ ,  $\text{N}_2\text{O}_4$ ,  $\text{H}_2\text{S}_2\text{O}_3$  and  $\text{H}_2\text{S}_2\text{O}_8$ , the total number of molecules containing covalent bond between two atoms of the same kind is \_\_\_\_\_ [JEE Adv. 2019]

**ANSWER-KEY****EXERCISE # I**

(ONLY ONE OPTION IS CORRECT)

| Que. | 1  | 2  | 3  | 4  | 5  | 6  | 7  | 8  | 9  | 10 |
|------|----|----|----|----|----|----|----|----|----|----|
| Ans. | C  | C  | B  | A  | B  | B  | D  | C  | B  | B  |
| Que. | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 |
| Ans. | A  | A  | A  | B  | B  | A  | B  | A  | A  | A  |
| Que. | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 |
| Ans. | B  | C  | B  | D  | A  | A  | B  | B  | C  | B  |
| Que. | 31 | 32 | 33 | 34 | 35 | 36 | 37 | 38 | 39 | 40 |
| Ans. | A  | D  | A  | B  | C  | C  | B  | C  | B  | D  |
| Que. | 41 | 42 | 43 | 44 | 45 | 46 | 47 |    |    |    |
| Ans. | A  | A  | B  | C  | A  | C  | A  |    |    |    |

**EXERCISE # II**

(ONE OR MORE THAN ONE OPTION MAY BE CORRECT)

| Que. | 1          | 2       | 3       | 4          | 5       | 6       | 7          | 8       | 9          | 10      |
|------|------------|---------|---------|------------|---------|---------|------------|---------|------------|---------|
| Ans. | A, B       | A, B, C | A, C, D | A, B, C    | A, B, D | A, B    | A, B, C    | A, B, C | A, B, C, D | A, C, D |
| Que. | 11         | 12      | 13      | 14         | 15      | 16      | 17         |         |            |         |
| Ans. | A, B, C, D | C, D    | C, D    | A, B, C, D | D       | B, C, D | A, B, C, D |         |            |         |

**EXERCISE # III**

PARAGRAPH &amp; MATRIX MATCH

| Que. | 1       | 2  | 3  | 4  | 5  | 6  | 7  | 8  | 9  | 10 |
|------|---------|----|----|----|----|----|----|----|----|----|
| Ans. | B       | A  | D  | A  | C  | D  | A  | B  | A  | A  |
| Que. | 11      | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 |
| Ans. | D       | C  | B  | C  | B  | B  | C  | A  | D  | C  |
| Que. | 21      | 22 | 23 | 24 |    |    |    |    |    |    |
| Ans. | B, C, D | B  | A  | B  |    |    |    |    |    |    |

**EXERCISE # J- MAINS**

| Que. | 1  | 2  | 3  | 4  | 5  | 6  | 7  | 8  | 9  | 10 |
|------|----|----|----|----|----|----|----|----|----|----|
| Ans. | 4  | 4  | 2  | 3  | 4  | 2  | 2  | 2  | 2  | 3  |
| Que. | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 |
| Ans. | 2  | 3  | 3  | 1  | 4  | 3  | 2  | 3  | 3  | 2  |
| Que. | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 |
| Ans. | 3  | 4  | 2  | 1  | 3  | 4  | 2  | 2  | 3  | 1  |
| Que. | 31 | 32 | 33 | 34 | 35 | 36 | 37 | 38 | 39 | 40 |
| Ans. | 3  | 1  | 1  | 3  | 4  | 4  | 2  | 2  | 3  | 2  |
| Que. | 41 | 42 | 43 | 44 | 45 | 46 | 47 | 48 | 49 | 50 |
| Ans. | 2  | 2  | 4  | 4  | 2  | 1  | 3  | 3  | 3  | 3  |
| Que. | 51 | 52 | 53 | 54 |    |    |    |    |    |    |
| Ans. | 4  | 1  | 2  | 4  |    |    |    |    |    |    |

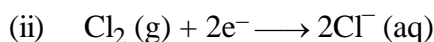
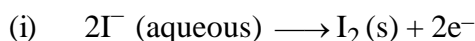
## EXERCISE # J-ADVANCED

## FILL IN THE BLANKS :

1. In nitrogen, d-orbitals are not present, so in it the possibility of intramolecular multiplicity exists which leads to the completion of octet through  $\pi$ -bond between two nitrogen atoms.

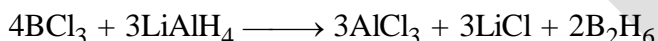
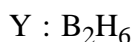
In phosphorus, d-orbitals are present, so in it due to large size of P, the P-P bonds are longer and hence intramolecular multiplicity is ruled out. So, for the completion of octet, it forms the bonds with three other 'P' atoms. Hence due to this reason it shows molecular formula as  $P_4$ .

2.  $2I^-$  (aqueous) +  $Cl_2 \longrightarrow I_2 + 2Cl^-$  (aqueous)

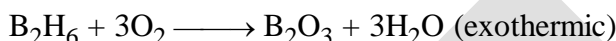


Thus,  $I^-$  is oxidised into  $I_2$  by  $Cl_2$  due to higher oxidised potential of  $Cl_2$  than  $I_2$

3. X :  $BCl_3$

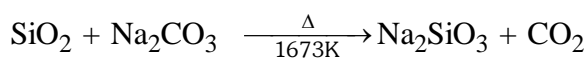
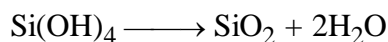
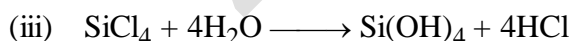
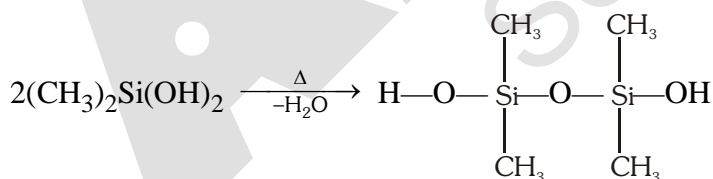
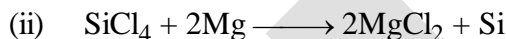


X

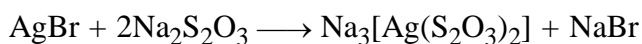


Y

4. (i)  $3SiCl_4 + 4Al \longrightarrow 3Si + 4AlCl_3$  (in one step)

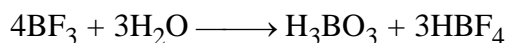


5. Unreacted AgBr is removed by hypo ( $Na_2S_2O_3$ )



6.  $^{14}\text{CO}_2$
7. (i)  $\text{Al}_4\text{Cl}_3 + 12\text{H}_2\text{O} \longrightarrow 4\text{Al}(\text{OH})_3 + 3\text{CH}_4 \uparrow$   
 (ii)  $\text{CaNCN} + 3\text{H}_2\text{O} \longrightarrow \text{CaCO}_3 \downarrow + 2\text{NH}_3$   
 (iii)  $4\text{BF}_3 + 3\text{H}_2\text{O} \longrightarrow \underset{\text{boric acid}}{\text{H}_3\text{BO}_3} + \underset{\text{fluoboric acid}}{3\text{HBF}_4}$   
 (iv)  $\text{NCl}_3 + 3\text{H}_2\text{O} \longrightarrow \text{NH}_3 + \underset{\text{hypochlorous acid}}{3\text{HOCl}}$   
 (v)  $2\text{XeF}_4 + 3\text{H}_2\text{O} \longrightarrow \text{Xe} + \underset{\text{xenon trioxide}}{\text{XeO}_3} + \text{F}_2 + 6\text{HCl}$

8. (i)  $\text{Al}_4\text{C}_3 + 12\text{H}_2\text{O} \longrightarrow 4\text{Al}(\text{OH})_3 + 3\text{CH}_4$   
 (ii)  $\text{CaNCN} + 3\text{H}_2\text{O} \longrightarrow \text{CaCO}_3 + 2\text{NH}_3$   
 (iii)  $\text{BF}_3 + 3\text{H}_2\text{O} \longrightarrow \text{H}_3\text{BO}_3 + 3\text{HF}$   
 $3\text{HF} + 3\text{BF}_3 \longrightarrow 3\text{HBF}_4$



9. Oxidation state

- (A) :  $\text{NaHSO}_3$  + 4  
 (B) :  $\text{Na}_2\text{SO}_3$  + 4  
 (C) :  $\text{Na}_2\text{S}_2\text{O}_3$  + 2  
 (D) :  $\text{Na}_2\text{S}_4\text{O}_6$  + 2.5

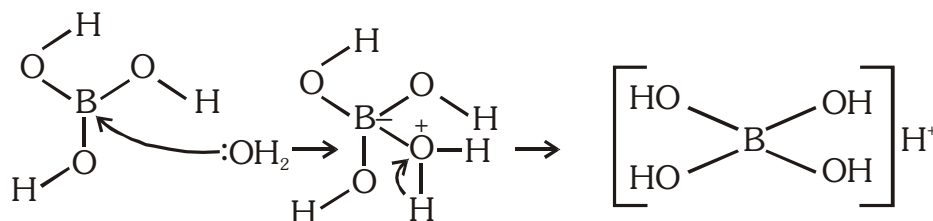
10.  $\text{Cl}_2\text{O}_7 < \text{SO}_3 < \text{CO}_2 < \text{B}_2\text{O}_3 < \text{BaO}$

OBJECTIVE TYPE :

- |                                                                                                    |       |       |       |           |       |
|----------------------------------------------------------------------------------------------------|-------|-------|-------|-----------|-------|
| 11. D                                                                                              | 12. A | 13. A | 14. C | 15. A,B,D | 16. A |
| 17. C                                                                                              | 18. D | 19. C | 20. C | 21. D     | 22. A |
| 23. A                                                                                              | 24. A |       |       |           |       |
| 25. (A) $\rightarrow$ Q, S ; (B) $\rightarrow$ R, S ; (C) $\rightarrow$ P ; (D) $\rightarrow$ Q, R |       |       |       |           |       |
| 26. C                                                                                              | 27. C | 28. B | 29. C | 30. B     | 31. A |
| 32. D                                                                                              | 33. A |       |       |           |       |

Boron always forms covalent bond because boron requires very high energy of form  $\text{B}^{3+}$  and again  $\text{B}^{3+}$  due to its very small size having high polarising power thus cause greater polarisation and eventually significant covalent characteristics-Fajans rule.

34. C



## Comprehension # 1 (Q. 35 to 37)

35. A                      36. C                      37. A or B

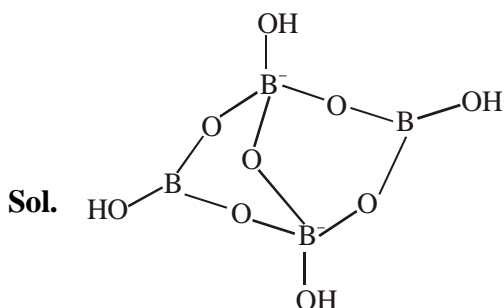
## Comprehension # 2 (Q.38 to 40)

38. C                      39. C                      40. B                      41. B                      42. C                      43. A  
 44. B,D                      45. B                      46. A,C,D                      47. A                      48. A                      49. D  
 50. C                      51. A                      52. B,D                      53. B,C                      54. B,C,D                      55. B  
 56. 6  
 57. (B)

Sol. The order of radius of 13<sup>th</sup> group elements is  $\text{Ga} < \text{Al} < \text{In} < \text{Tl}$ .

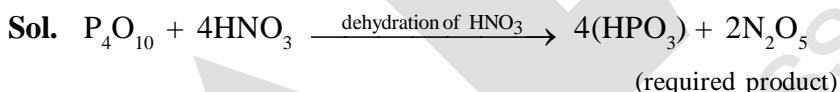
Reason  $\Rightarrow$  Due to poor shielding effect of d-orbital, radius of Ga is smaller than Al.

58. (A,C,D)

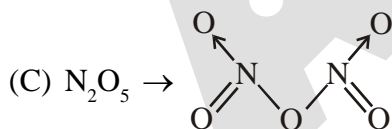


- (A) Having  $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$  tetranuclear (boron) unit  
 (B) All boron atoms not in same plane  
 (C) Two boron are  $\text{sp}^2$  hybridised and two boron are  $\text{sp}^3$  hybridised  
 (D) One terminal hydroxide per boron atom is present.

59. (B,D)



- (A)  $\text{P}_4 + 20\text{HNO}_3 \rightarrow 4\text{H}_3\text{PO}_4 + 20\text{NO}_2\uparrow + 4\text{H}_2\text{O}$   
 (B)  $\text{N}_2\text{O}_5$  is diamagnetic in nature



$\text{N}_2\text{O}_5$  contains one N–O–N bond not N–N bond.

- (D)  $\text{Na} + \text{N}_2\text{O}_5 \rightarrow \text{NaNO}_3 + \text{NO}_2\uparrow$   
 (Brown gas)

60. A,C,D                      61. B,C                      62. A                      63. C,D  
 64. A,C,D                      65. B                      66. C                      67. B,C  
 68. 5 or 6                      69. (1,4)                      70. (19.00)                      71. (288.00)  
 72. (2,4)                      73. (4.00)



## Important Notes

## SURFACE CHEMISTRY

### 1. INTRODUCTION

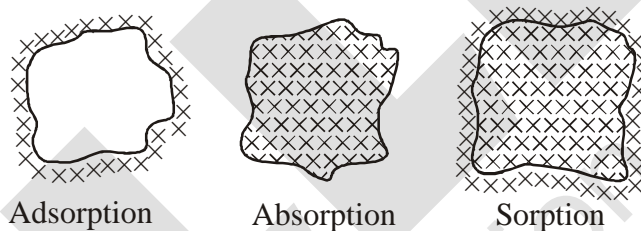
Surface chemistry deals with phenomena that occur at the surfaces or interfaces. The interface or surface is represented by separating the bulk phases by a hyphen or a slash. For example, the interface between a solid and a gas may be represented by solid-gas or solid/gas. Due to complete miscibility, there is no interface between the gases. The bulk phases that we come across in surface chemistry may be pure compounds or solutions. The interface is normally a few molecules thick but its area depends on the size of the particles of bulk phases. Many important phenomena, noticeable amongst these being corrosion, electrode processes, heterogeneous catalysis, dissolution and crystallisation occur at interfaces.

### 2. ADSORPTION

The tendency of accumulation of molecular species at the surface than in the bulk of a solid (or liquid) is termed **adsorption**. The molecular species or substance which concentrates or accumulates at the surface is termed **adsorbate** and the material on whose surface the adsorption has taken place is called **adsorbent**.

#### 2.1 DISTINCTION BETWEEN ADSORPTION AND ABSORPTION :

In adsorption the concentration of the adsorbate increases only at the surface of the adsorbent, while in absorption the concentration is uniform throughout the bulk of the solid.



There are several examples, which reveal that the surface of a solid has the tendency to attract and retain the molecules of the phase with which it comes into contact. These molecules remain only at the surface and do not go deeper into the bulk. Adsorption is essentially a surface phenomenon. Solids, particularly in finely divided state, have large surface area and therefore, charcoal, silica gel, alumina gel, clay, colloids, metals in finely divided state, etc. act as good adsorbents.

- (i) In adsorption, the composition of final sample at surface & bulk will differ largely, while in absorption, the composition will be nearly same.
- (ii) The rate of adsorption decreases with time but absorption occurs at nearly constant rate.
- (iii) Adsorption is always exothermic but absorption may be endothermic or exothermic.

#### Adsorption in action :

- (i) If a gas like  $O_2$ ,  $H_2$ ,  $CO$ ,  $Cl_2$ ,  $NH_3$  or  $SO_2$  is taken in a closed vessel containing powdered charcoal, it is observed that the pressure of the gas in the enclosed vessel decreases. The gas molecules concentrate at the surface of the charcoal, i.e., gases are adsorbed at the surface.
- (ii) In a solution of an organic dye, say methylene blue, when animal charcoal is added and the solution is well shaken, it is observed that the filtrate turns colourless. The molecules of the dye, thus, accumulate on the surface of charcoal, i.e., are adsorbed.

- (iii) Aqueous solution of raw sugar, when passed over beds of animal charcoal, becomes colourless as the colouring substances are adsorbed by the charcoal.
- (iv) The air becomes dry in the presence of silica gel because the water molecules get adsorbed on the surface of the gel.

In absorption as well as adsorption, the concentration or partial pressure of adsorbate or adsorbate, decreases.

**Ex. 1.** A vessel of capacity 8.21L contains  $\text{NH}_3$  gas at 1.5 atm and  $27^\circ\text{C}$ . Now, 5 gm charcoal is added in the vessel and left for sufficient time. After sufficient time, the pressure of gas decreased to 1.2 atm. Calculate the mass of  $\text{NH}_3$  gas adsorbed per gm of charcoal. Neglect the volume of charcoal.

**Sol.**  $\text{Mass of NH}_3 \text{ gas adsorbed} = \frac{\Delta P \cdot V \cdot M}{RT} = \frac{0.3 \times 8.21 \times 17}{0.0821 \times 300} = 1.7 \text{ gm}$

$\therefore \text{Mass of NH}_3 \text{ gas adsorbed per gm of charcoal} = \frac{1.7}{5} = 0.34 \text{ gm}$

## 2.2 MECHANISM OF ADSORPTION :

Adsorption is due to the fact that the surface particles of the adsorbent are in different state than the particles inside the bulk.

- (i) Inside the adsorbent all the force acting between the particles are mutually balanced but on the surface the particles are not surrounded by atoms or molecules of their kind on all sides and hence they possess **Unbalanced or residual attractive force**. These forces of the adsorbent are responsible for attracting the adsorbate particle on its surface.
- (ii) Another important factor featuring adsorption is the heat of adsorption. During adsorption, there is always a decrease in residual forces of the surface, i.e., there is decrease in surface energy which appears as heat. Adsorption, therefore, is invariably an exothermic process. In other words,  $\Delta H$  of adsorption is always negative. When a gas is adsorbed, the freedom of movement of its molecules become restricted. This amounts to decrease in the entropy of the gas after adsorption, i.e.,  $\Delta S$  is negative. Adsorption is thus accompanied by decrease in enthalpy as well as decrease in entropy of the system. For a process to be spontaneous, the thermodynamic requirement is that, at constant temperature and pressure,  $\Delta G$  must be negative, i.e., there is a decrease in Gibbs energy. On the basis of equation,  $\Delta G = \Delta H - T\Delta S$ ,  $\Delta G$  can be negative if  $\Delta H$  has sufficiently high negative value as  $-T\Delta S$  is positive. Thus, in an adsorption process, which is spontaneous, a combination of these two factors makes  $\Delta G$  negative. As the adsorption proceeds,  $\Delta H$  becomes less and less negative ultimately  $\Delta H$  becomes equal to  $T\Delta S$  and  $\Delta G$  becomes zero. At this state equilibrium is attained.

The adsorbate particles may undergo the following further activity :

- (i) If nature & condition will favour, they will diffuse in bulk resulting in adsorption.
- (ii) They may move at the surface.
- (iii) They come out of the surface resulting desorption.

Normally, desorption follows I order kinetics & obeys Arrhenius equation.

**Ex.2.** Calculate the time upto which a hydrogen molecule may remain absorbed at pt surface at 500 K. ( $A = 14 \times 10^{15} \text{ sec}^{-1}$ ,  $E_a = 10 \text{ kcal/mole}$ )

**Sol.** 
$$T_{av} = \frac{1}{1.4 \times 10^{15} e^{-10}} = \frac{e^{10}}{1.4 \times 10^{15}}$$

### 2.3 TYPES OF ADSORPTION :

There are two main types of adsorption of gases on solids.

**(i) Physical adsorption or physisorption :**

In this adsorption, accumulation of gas on the surface of a solid occurs on account of weak VanderWaals' force.

**(ii) Chemical adsorption or chemisorption.**

The gas molecules or atoms are held to the solid surface by chemical bonds (covalent or ionic) in nature. Chemisorption has high energy of activation and is, therefore, often referred as **activated adsorption**.

Sometimes these two processes occur simultaneously and it is not easy to ascertain the type of adsorption.

**Note :**

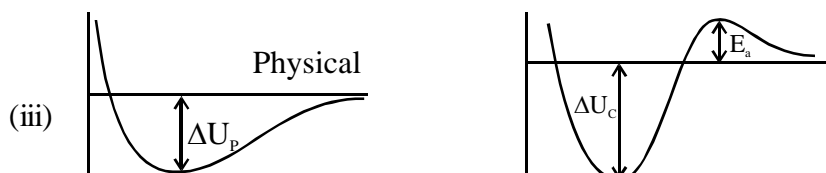
A physical adsorption at low temperature may pass into chemisorption as the temperature is increased. For example, hydrogen is first adsorbed on nickel by van der Waals' force. Molecules of hydrogen then dissociate and hydrogen atoms are held on the surface by chemisorption.

### COMPARISON OF CHARACTERISTICS OF PHYSISORPTION AND CHEMISORPTION

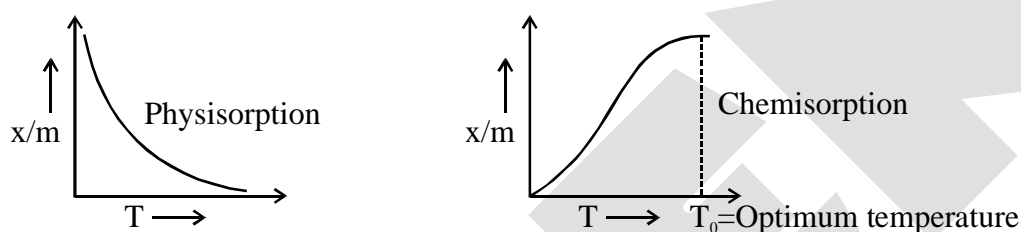
|   | PHYSICAL ADSORPTION                                                                  | CHEMICAL ADSORPTION                                                                                    |
|---|--------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------|
| 1 | It is caused by weak forces.                                                         | It is caused by chemical bond formation                                                                |
| 2 | It is not specific.                                                                  | It is highly specific (Bond formation is necessary)                                                    |
| 3 | It is reversible.                                                                    | It is irreversible.                                                                                    |
| 4 | It depends on the nature of gas. More easily liquefiable gases are adsorbed readily. | It depends on the nature of gas. Gases which form compounds with the adsorbent exhibit chemi-sorption. |
| 5 | Enthalpy of adsorption is low ( $20-40 \text{ kJ mol}^{-1}$ )                        | Enthalpy of adsorption is low ( $80-240 \text{ kJ mol}^{-1}$ )                                         |
| 6 | Low temperature is favourable. It decreases with increase of temperature.            | High temperature is favourable. It increases with the increase in temperature upto certain limit.      |
| 7 | No appreciable activation energy is involved.                                        | High activation energy is involved.                                                                    |
| 8 | High pressure is favourable. Decrease of pressure causes desorption.                 | High pressure is favourable. Decrease of pressure does not cause desorption.                           |
| 9 | It forms multilayers on adsorbent surface under high pressure.                       | It forms unimolecular layer.                                                                           |

**Note :**

- (i) Chemisorption is irreversible. Either desorption does not occur or molecules other than adsorbate leave the surface.
- (ii) Chemisorption is more exothermic & hence its  $E_a$  should be negligible. But in reality it is high due to requirement of bond cleavage in the adsorbate molecule before adsorption. Due to higher  $E_a$ , it is called **activated adsorption**.



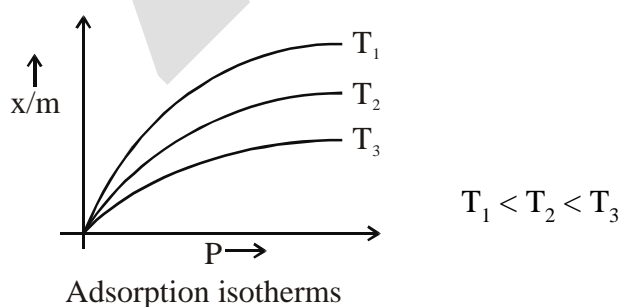
- (iv) On increasing temperature, the extent of physisorption decreases but chemisorption increases.



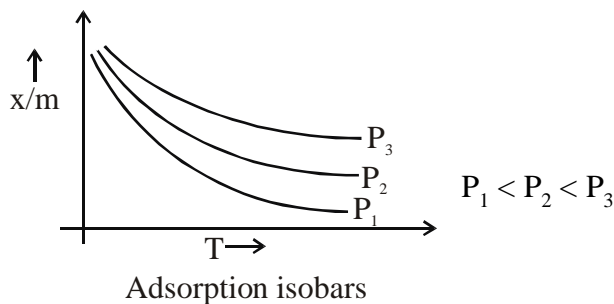
$x$  : mass of adsorbate  
and  $m$  : mass of adsorbent

**2.4 FACTORS AFFECTING ADSORPTION OF GASES ON SOLIDS :**

- (i) **Nature of gas :** Easily liquifiable gases (having higher critical temperature) adsorb to the greater extent.
- (ii) **Nature of adsorbent :** Specific surface area represent the surface area of adsorbent per unit mass. Greater the specific surface area, more will be the adsorption. Charcoal, silica gel, alumina gel, colloids are good adsorbents.
- (iii) **Surface area :** Adsorption increases on increasing the surface area.
- (iv) **Pressure :** Adsorption of gas at solid surface (increases due to) decrease in volume of system & hence extent of adsorption increases on increasing pressure.



(v) Temperature :  $T \uparrow$       Physisorption  $\downarrow$       Chemisorption  $\uparrow$



### 2.4.1 Freundlich adsorption isotherm :

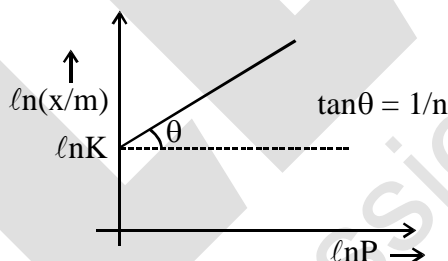
Freundlich, in 1909, gave an empirical relationship between the quantity of gas adsorbed ( $x$ ) by unit mass of solid adsorbent ( $m$ ) and pressure at a particular temperature. The relationship can be expressed by the following equation.

$$\frac{x}{m} = K \cdot P^{1/n} \quad (n \geq 1)$$

where  $K$  &  $n$  are constant, depending on nature of gas, solid & temperature.

For any combination of gas, solid & temperature, the values of  $k$  &  $n$  may be determined graphically.

$$\ln\left(\frac{x}{m}\right) = \ln K + \frac{1}{n} \ln P$$

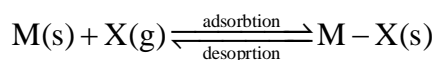


Freundlich isotherm is straight line. Freundlich isotherm fails at high pressure.

### 2.4.2 Langmuir's adsorption isotherm :

He derived the condition of equilibrium theoretically assuming that adsorption is

- monolayer
- uniform at solid surface
- adsorbate particles do not interact each other at the surface.



At any instant :

Rate of adsorption,  $r_a \propto P$

$$\propto (1 - \theta)$$

$$\therefore r_a = K_a P(1 - \theta)$$

where,  $\theta$  = Fraction of surface area already occupied by adsorbate particles.

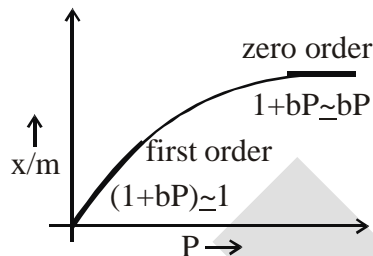
and Rate of desorption,  $r_d \propto \theta \Rightarrow r_d = K_d \cdot \theta$

At eqb.  $r_a = r_d$

$$\theta = \frac{K_a P}{K_d + K_a P} = \frac{\cancel{K_a} P}{1 + \cancel{K_a} / \cancel{K_d} P} = \frac{K_{eq} P}{1 + K_{eq} P}$$

Now,  $\frac{x}{m} \propto \theta$

$$\frac{x}{m} = K\theta = K \frac{K_{eq} P}{1 + K_{eq} P} = \frac{aP}{1 + bP} \quad a, b = \text{constant}$$



## 2.5 ADSORPTION FROM SOLUTION PHASE :

Solids can adsorb solutes from solutions also. When a solution of acetic acid in water is shaken with charcoal, a part of the acid is adsorbed by the charcoal and the concentration of the acid decreases in the solution. Similarly, the litmus solution when shaken with charcoal becomes colourless. The precipitate of  $\text{Mg}(\text{OH})_2$  attains blue colour when precipitated in presence of magneson reagent. The colour is due to adsorption of magneson. The following observations have been made in the case of adsorption from solution phase:

- The extent of adsorption decreases with an increase in temperature.
- The extent of adsorption increases with an increase of surface area of the adsorbent.
- The extent of adsorption depends on the concentration of the solute in solution.
- The extent of adsorption depends on the nature of the adsorbent and the adsorbate.

The precise mechanism of adsorption from solution is not known. Freundlich's equation approximately describes the behaviour of adsorption from solution with a difference that instead of pressure, concentration of the solution is taken into account, i.e.,

$$\frac{x}{m} = kC^{1/n}$$

(C is the equilibrium concentration, i.e., when adsorption is complete).

On taking logarithm of the above equation, we have

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log C$$

Plotting  $\log \frac{x}{m}$  against  $\log C$  a straight line is obtained which shows the validity of Freundlich isotherm.

This can be tested experimentally by taking solutions of different concentrations of acetic acid. Equal volumes of solutions are added to equal amounts of charcoal in different flasks. The final concentration is determined in each flask after adsorption. The difference in the initial and final concentrations give the value of  $x$ . Using the above equation, validity of Freundlich isotherm can be established.

## 2.6 APPLICATIONS OF ADSORPTION :

The phenomenon of adsorption finds a number of applications. Important ones are listed here:

(i) **Production of high vacuum :**

The remaining traces of air can be adsorbed by charcoal from a vessel evacuated by a vacuum pump to give a very high vacuum.

(ii) **Gas masks:**

Gas mask (a device which consists of activated charcoal or mixture of adsorbents) is usually used for breathing in coal mines to adsorb poisonous gases.

(iii) **Control of humidity:**

Silica and aluminium gels are used as adsorbents for removing moisture and controlling humidity.

(iv) **Removal of colouring matter from solutions:**

Animal charcoal removes colours of solutions by adsorbing coloured impurities.

(v) **Heterogeneous catalysis:**

Adsorption of reactants on the solid surface of the catalysts increases the rate of reaction. There are many gaseous reactions of industrial importance involving solid catalysts. Manufacture of ammonia using iron as a catalyst, manufacture of  $\text{H}_2\text{SO}_4$  by contact process and use of finely divided nickel in the hydrogenation of oils are excellent examples of heterogeneous catalysis.

(vi) **Separation of inert gases:**

Due to the difference in degree of adsorption of gases by charcoal, a mixture of noble gases can be separated by adsorption on coconut charcoal at different temperatures.

(vii) **In curing diseases:** A number of drugs are used to kill germs by getting adsorbed on them.

(viii) **Froth floatation process:**

A low grade sulphide ore is concentrated by separating it from silica and other earthy matter by this method using pine oil and frothing agent

(ix) **Adsorption indicators:**

Surfaces of certain precipitates such as silver halides have the property of adsorbing some dyes like eosin, fluorescein, etc. and thereby producing a characteristic colour at the end point.

(x) **Chromatographic analysis:**

Chromatographic analysis based on the phenomenon of adsorption finds a number of applications in analytical and industrial fields.

## 3. CATALYSIS

The systematic study of the effect of various foreign substances on the rates of chemical reactions was first made by Berzelius, in 1835. He suggested the term catalyst for such substances. Substances, which accelerate the rate of a chemical reaction and themselves remain chemically and quantitatively unchanged after the reaction, are known as catalysts, and the phenomenon is known as catalysis.



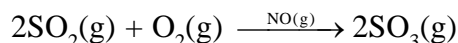
### 3.1 HOMOGENEOUS AND HETEROGENEOUS CATALYSIS :

Catalysis can be broadly divided into two groups:

#### (a) Homogeneous catalysis :

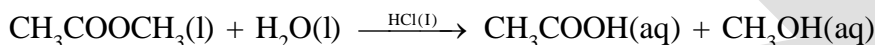
When the reactants and the catalyst are in the same phase (i.e., liquid or gas), the process is said to be homogeneous catalysis. The following are some of the examples of homogeneous catalysis:

- (i) Oxidation of sulphur dioxide into sulphur trioxide with dioxygen in the presence of oxides of nitrogen as the catalyst in the lead chamber process.



The reactants, sulphur dioxide and oxygen, and the catalyst, nitric oxide, are all in the same phase.

- (ii) Hydrolysis of methyl acetate is catalysed by  $\text{H}^+$  ions furnished by hydrochloric acid.

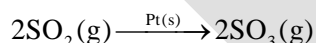


Both the reactants and the catalyst are in the same phase.

### 3.2 HETEROGENEOUS CATALYSIS :

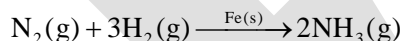
The catalytic process in which the reactants and the catalyst are in different phases is known as heterogeneous catalysis. Some of the examples of heterogeneous catalysis are given below:

- (i) Oxidation of sulphur dioxide into sulphur trioxide in the presence of Pt.



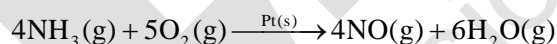
The reactant is in gaseous state while the catalyst is in the solid state.

- (ii) Combination between dinitrogen and dihydrogen to form ammonia in the presence of finely divided iron in Haber's process.



The reactants are in gaseous state while the catalyst is in the solid state.

- (iii) Oxidation of ammonia into nitric oxide in the presence of platinum gauze in Ostwald's process.



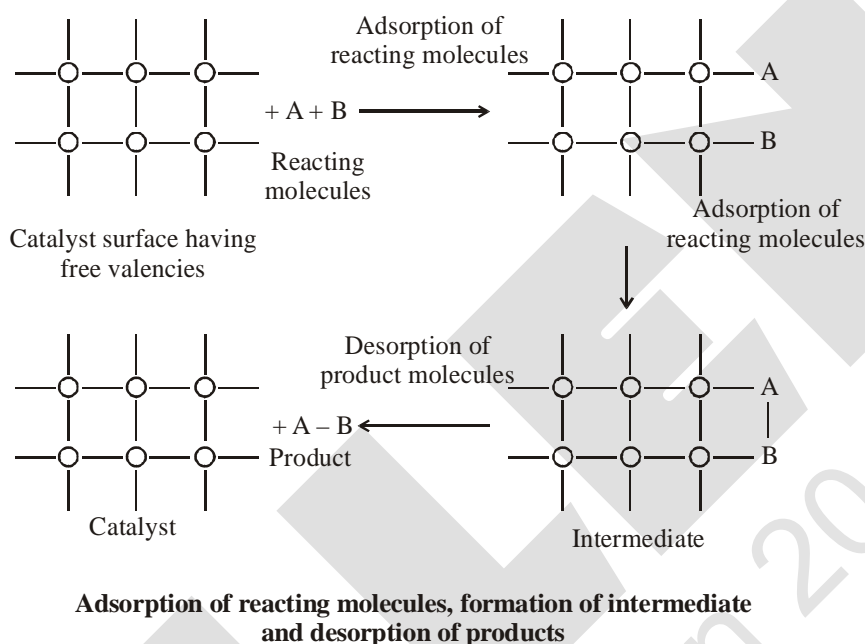
The reactants are in gaseous state while the catalyst is in the solid state

#### Adsorption Theory of Heterogeneous Catalysis :

This theory explains the mechanism of heterogeneous catalysis. The old theory, known as adsorption theory of catalysis, was that the reactants in gaseous state or in solutions, are adsorbed on the surface of the solid catalyst. The increase in concentration of the reactants on the surface increases the rate of reaction. Adsorption being an exothermic process, the heat of adsorption is utilised in enhancing the rate of the reaction. The modern adsorption theory is the combination of intermediate compound formation theory and the old adsorption theory. The catalytic activity is localised on the surface of the catalyst. The mechanism involves five steps:

- Diffusion of reactants to the surface of the catalyst.
- Adsorption of reactant molecules on the surface of the catalyst.
- Occurrence of chemical reaction on the catalyst's surface through formation of an intermediate
- Desorption of reaction products from the catalyst surface, and thereby, making the surface available again for more reaction to occur.

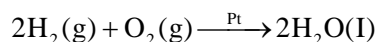
- (v) Diffusion of reaction products away from the catalyst's surface. The surface of the catalyst unlike the inner part of the bulk, has free valencies which provide the seat for chemical forces of attraction. When a gas comes in contact with such a surface, its molecules are held up there due to loose chemical combination. If different molecules are adsorbed side by side, they may react with each other resulting in the formation of new molecules. Thus, formed molecules may evaporate leaving the surface for the fresh reactant molecules. This theory explains why the catalyst remains unchanged in mass and chemical composition at the end of the reaction and is effective even in small quantities. It however, does not explain the action of catalytic promoters and catalytic poisons.



### 3.3 IMPORTANT FEATURES OF SOLID CATALYSTS :

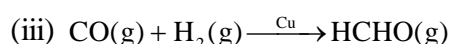
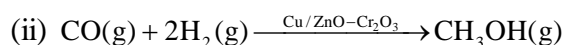
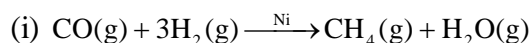
#### (a) Activity :

The activity of a catalyst depends upon the strength of chemisorption to a large extent. The reactants must get adsorbed reasonably strongly on to the catalyst to become active. However, they must not get adsorbed so strongly that they are immobilised and other reactants are left with no space on the catalyst's surface for adsorption. It has been found that for hydrogenation reaction, the catalytic activity increases from Group 5 to Group 11 metals with maximum activity being shown by groups 7-9 elements of the periodic table



#### (b) Selectivity :

The selectivity of a catalyst is its ability to direct a reaction to yield a particular product. For example, starting with  $\text{H}_2$  and  $\text{CO}$ , and using different catalysts, we get different products.



Thus, it can be inferred that the action of a catalyst is highly selective in nature, i.e., a given substance can act as a catalyst only in a particular reaction and not for all the reactions.

### 3.4 SHAPE-SELECTIVE CATALYSIS BY ZEOLITES :

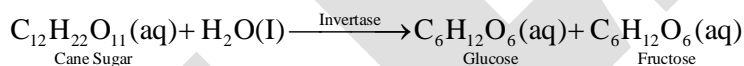
The catalytic reaction that depends upon the pore structure of the catalyst and the size of the reactant and product molecules is called shape-selective catalysis. Zeolites are good shape-selective catalysts because of their honeycomb-like structures. They are microporous aluminosilicates with three dimensional network of silicates in which some silicon atoms are replaced by aluminium atoms giving Al–O–Si framework. The reactions taking place in zeolites depend upon the size and shape of reactant and product molecules as well as upon the pores and cavities of the zeolites.

They are found in nature as well as synthesised for catalytic selectivity. Zeolites are being very widely used as catalysts in petrochemical industries for cracking of hydrocarbons and isomerisation. An important zeolite catalyst used in the petroleum industry is ZSM-5. It converts alcohols directly into gasoline (petrol) by dehydrating them to give a mixture of hydrocarbons.

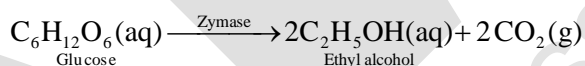
### 3.5 ENZYME CATALYSIS :

Enzymes are complex nitrogenous organic compounds which are produced by living plants and animals. They are actually protein molecules of high molecular mass and form colloidal solutions in water. They are very effective catalysts, numerous reactions that occur in the bodies of animals and plants to maintain the life process are catalysed by enzymes. The enzymes are, thus, termed as **biochemical catalysts** and the phenomenon is known as **biochemical catalysis**. Many enzymes have been obtained in pure crystalline state from living cells. However, the first enzyme was synthesised in the laboratory in 1969. The following are some of the examples of enzyme-catalysed reactions:

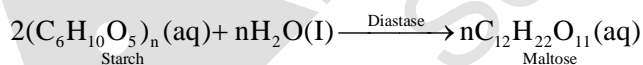
- (i) Inversion of cane sugar: The invertase enzyme converts cane sugar into glucose and fructose.



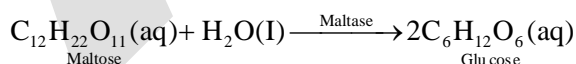
- (ii) Conversion of glucose into ethyl alcohol: The zymase enzyme converts glucose into ethyl alcohol and carbon dioxide.



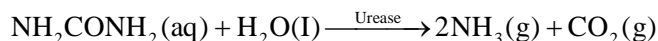
- (iii) Conversion of starch into maltose: The diastase enzyme converts starch into maltose.



- (iv) Conversion of maltose into glucose: The maltase enzyme converts maltose into glucose.



- (v) Decomposition of urea into ammonia and carbon dioxide: The enzyme urease catalyses this decomposition.



- (vi) In stomach, the pepsin enzyme converts proteins into peptides while in intestine, the pancreatic trypsin converts proteins into amino acids by hydrolysis.

- (vii) Conversion of milk into curd: It is an enzymatic reaction brought about by lacto bacilli enzyme present in curd.

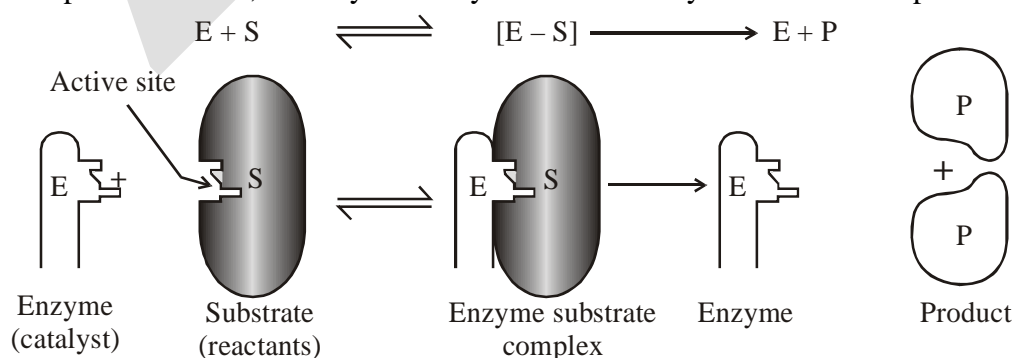
### 3.5.1 Characteristics of enzyme catalysis :

Enzyme catalysis is unique in its efficiency and high degree of specificity. The following characteristics are exhibited by enzyme catalysts:

- (i) Most highly efficient: One molecule of an enzyme may transform one million molecules of the reactant per minute.
- (ii) Highly specific nature: Each enzyme is specific for a given reaction, i.e., one catalyst cannot catalyse more than one reaction. For example, the enzyme urease catalyses the hydrolysis of urea only. It does not catalyse hydrolysis of any other amide.
- (iii) Highly active under optimum temperature: The rate of an enzyme reaction becomes maximum at a definite temperature, called the optimum temperature. On either side of the optimum temperature, the enzyme activity decreases. The optimum temperature range for enzymatic activity is 298-310K. Human body temperature being 310 K is suited for enzyme-catalysed reactions.
- (iv) Highly active under optimum pH: The rate of an enzyme-catalysed reaction is maximum at a particular pH called optimum pH, which is between pH values 5-7.
- (v) Increasing activity in presence of activators and co-enzymes: The enzymatic activity is increased in the presence of certain substances, known as co-enzymes. It has been observed that when a small non-protein (vitamin) is present along with an enzyme, the catalytic activity is enhanced considerably. Activators are generally metal ions such as  $\text{Na}^+$ ,  $\text{Mn}^{2+}$ ,  $\text{CO}^{2+}$ ,  $\text{Cu}^{2+}$ , etc. These metal ions, when weakly bonded to enzyme molecules, increase their catalytic activity. Amylase in presence of sodium chloride i.e.,  $\text{Na}^+$  ions are catalytically very active.
- (vi) Influence of inhibitors and poisons: Like ordinary catalysts, enzymes are also inhibited or poisoned by the presence of certain substances. The inhibitors or poisons interact with the active functional groups on the enzyme surface and often reduce or completely destroy the catalytic activity of the enzymes. The use of many drugs is related to their action as enzyme inhibitors in the body.

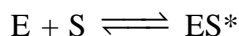
### 3.5.2 Mechanism of enzyme catalysis :

There are a number of cavities present on the surface of colloidal particles of enzymes. These cavities are of characteristic shape and possess active groups such as  $-\text{NH}_2$ ,  $-\text{COOH}$ ,  $-\text{SH}$ ,  $-\text{OH}$ , etc. These are actually the active centres on the surface of enzyme particles. The molecules of the reactant (substrate), which have complementary shape, fit into these cavities just like a key fits into a lock. On account of the presence of active groups, an activated complex is formed which then decomposes to yield the products. Thus, the enzyme-catalysed reactions may be considered to proceed in two steps.

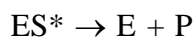


**3.5.3 Mechanism of enzyme catalysed reaction :**

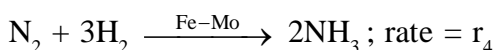
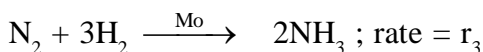
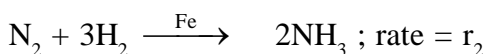
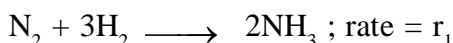
**Step 1:** Binding of enzyme to substrate to form an activated complex.



**Step 2:** Decomposition of the activated complex to form product.

**3.6 CATALYTIC PROMOTORS :**

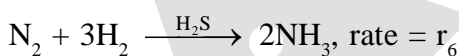
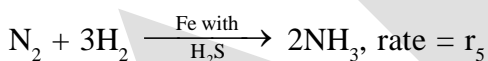
There are the substances, which are not the catalyst of that reaction but increases the activity of catalyst.



Experimentally,  $r_1 = r_3 < r_2 < r_4$ . It suggests that Mo is not catalyst of this reaction. But when it is mixed with iron, it increased the catalytic activity of iron. Hence, Mo is catalytic promotor in this reaction.

**3.7 CATALYTIC POISONS :**

These are the substances, which are not the catalyst of that reaction but decreases the activity of catalyst.

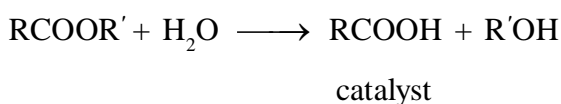


Experimentally,  $r_1 = r_6 < r_5 < r_2$ . It suggests that  $H_2S$  is not catalyst of reaction but it decreases the activity of Fe catalyst. Hence,  $H_2S$  is catalytic poison in this reaction.

**3.8 AUTO CATALYSIS :**

These are the reactions in which some of the product of reaction, catalyses the reaction.

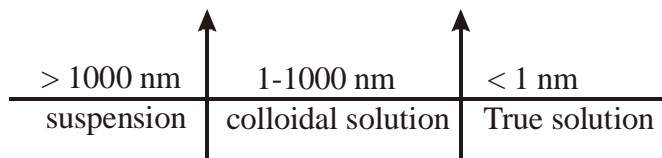
For example



#### 4. COLLOIDS

A colloid is a heterogeneous system in which one substance is dispersed (dispersed phase) as very fine particles in another substance called dispersion medium.

##### 4.1 PARTICLE SIZE :



##### 4.2 PHASE OF COLLOIDS :

A colloidal system is heterogeneous in character. It consists of two phases, namely a dispersed phase and a dispersion medium.

- (a) **Dispersed Phase :** It is the component present in small proportion and is just like a solute in a true solution. For example, in the colloidal state of sulphur in water, the former acts as a dispersed phase.
- (b) **Dispersion Medium :** It is normally the component present in excess and is just like a solvent in a solution.

The particles of the dispersed phase are scattered in the dispersion medium in a colloidal system.

##### 4.3 CLASSIFICATION OF COLLOIDS :

Colloids can be classified in a number of ways based upon some of their important characteristics.

##### 4.3.1 Physical state of Dispersed Phase & Dispersion Medium:

Depending upon whether the dispersed phase and the dispersion medium are solids, liquids or gaseous, eight types of colloidal system are possible.

**A gas mixed with another gas forms a homogeneous mixture and not a colloidal system.** Typical examples of various type alongwith their characteristic names are given in table.

Types of Colloidal Systems

| Dispersed phase | Dispersion medium | Type of colloid | Examples                             |
|-----------------|-------------------|-----------------|--------------------------------------|
| Solid           | Solid             | Solid sol       | Some coloured glasses and gem stones |
| Solid           | Liquid            | Sol             | Paints, cell fluids                  |
| Solid           | Gas               | Aerosol         | Smoke, dust                          |
| Liquid          | Solid             | Gel             | Cheese, butter, jellies              |
| Liquid          | Liquid            | Emulsion        | Milk, hair cream                     |
| Liquid          | Gas               | Aerosol         | Fog, mist, cloud, insecticide sprays |
| Gas             | Solid             | Solid sol       | Pumice stone, foam rubber.           |
| Gas             | Liquid            | Foam            | Froth, whipped cream, soap lather    |

- \* A colloidal system in which the dispersion medium is a liquid or gas are called sols. They are called hydrosols or aqua sols, if the dispersion medium is water. When the dispersion medium is alcohol or benzene, they are accordingly called alcosols or benzosol.

- \* Colloidal systems in which the dispersion medium is a gas are called aerosols.
- \* Colloids in which the dispersion medium is a solid are called gels, e.g. cheese etc. They have a more rigid structure. Some colloids, such as gelatin, can behave both as a sol and a gel. At high temperature and low concentration of gelatin, the colloid is a hydrosol. But at low temperature and high gelatin concentration, the hydrosol can change into a gel.

**4.3.2 Based on interaction or affinity of phases :** On the basis of the affinity or interaction between the dispersed phase and the dispersion medium, the colloids may be classified into two types :

- (i) **Lyophilic colloids :** The word 'lyophilic' means liquid-loving. Colloidal sols directly formed by mixing substances like gum, gelatine, starch, rubber, etc., with a suitable liquid (the dispersion medium) are called lyophilic sols. An important characteristic of these sols is that if the dispersion medium is separated from the dispersed phase (say by evaporation), the sol can be reconstituted by simply remixing with the dispersion medium. That is why these sols are also called reversible sols. Which are quite stable.
- (ii) **Lyophobic colloids :** The word 'lyophobic' means liquid-hating. Substances like metals, their sulphides, etc., when simply mixed with the dispersion medium do not form the colloidal sol. Their colloidal sols can be prepared only by special methods. Such sols are called lyophobic sols. These sols are readily precipitated (or coagulated) on the addition of small amounts of electrolytes, by heating or by shaking and hence, are not stable. Further, once precipitated, they do not give back the colloidal sol by simple addition of the dispersion medium. Hence, these sols are also called irreversible sols. Lyophobic sols need stabilising agents for their preservation.

**Difference between Lyophilic and Lyophobic sols**

| Property                       | Lyophilic sols                                                                                                                                    | Lyophobic sols                                                                                                    |
|--------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------|
| 1. Nature                      | Reversible                                                                                                                                        | Irreversible                                                                                                      |
| 2. Preparation                 | They are prepared very easily by shaking or warming the substance with dispersion medium. They do not required any electrolyte for stabilization. | They are difficult to prepare, Special methods are used. Addition of stabiliser is essential for their stability. |
| 3. Stability                   | They are very stable and are not easily coagulated by electrolytes.                                                                               | They are generally unstable and get easily coagulated on addition of electrolytes.                                |
| 4. Charge                      | Particles carry no or very little charge depending upon the pH of the medium.                                                                     | Colloidal particles have characteristic charge (positive or negative)                                             |
| 5. Viscosity                   | Viscosity is much higher than that of the medium.                                                                                                 | Viscosity is nearly the same as that of the medium                                                                |
| 6. Migration in electric field | The particles may or may not migrate in an electric field.                                                                                        | The colloidal particles migrate either towards cathode or anode in an electric field.                             |
| 7. Solvation                   | Particles are heavily solvated.                                                                                                                   | Particles are not solvated.                                                                                       |
| 8. Action of electrolyte       | Large amount of electrolyte is required to cause coagulation.                                                                                     | Small amount of electrolyte is sufficient to cause cogulation.                                                    |
| 9. Examples                    | Mostly organic substances e.g. starch, gums, proteins, gelatin etc.                                                                               | Generally inorganic substance e.g., metal sols, sulphides and oxides sols.                                        |

### 4.3.3 Classification Based on Type of Particles of the Dispersed Phase :

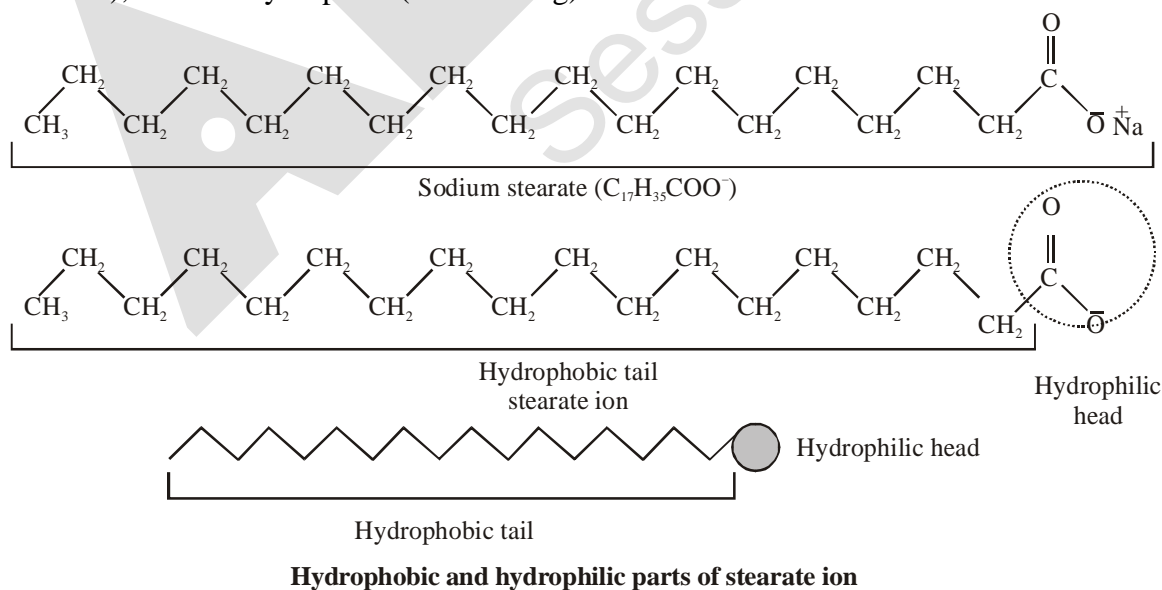
Depending upon the type of the particles of the dispersed phase, colloids are classified as: multimolecular, macromolecular and associated colloids.

- (i) **Multimolecular colloids:** On dissolution, a large number of atoms or smaller molecules of a substance aggregate together to form species having size in the colloidal range (diameter  $< 1 \text{ nm}$ ). The species thus formed are called multimolecular colloids. For example, a gold sol may contain particles of various sizes having many atoms. Sulphur sol consists of particles containing a thousand or more of  $\text{S}_8$  sulphur molecules.
- (ii) **Macromolecular colloids:** Macromolecules (Unit 15) in suitable solvents form solutions in which the size of the macromolecules may be in the colloidal range. Such systems are called macromolecular colloids. These colloids are quite stable and resemble true solutions in many respects. Examples of naturally occurring macromolecules are starch, cellulose, proteins and enzymes; and those of man-made macromolecules are polythene, nylon, polystyrene, synthetic rubber, etc.
- (iii) **Associated colloids (Micelles):** There are some substances which at low concentrations behave as normal strong electrolytes, but at higher concentrations exhibit colloidal behaviour due to the formation of aggregates. The aggregated particles thus formed are called micelles. These are also known as associated colloids.

The formation of micelles takes place only above a particular temperature called **Kraft temperature** ( $T_k$ ) and above a particular concentration called **critical micelle concentration** (CMC). On dilution, these colloids revert back to individual ions. Surface active agents such as soaps and synthetic detergents belong to this class. These colloids have both lyophobic and lyophilic parts. Micelles may contain as many as 100 molecules or more.

#### Mechanism of micelle formation :

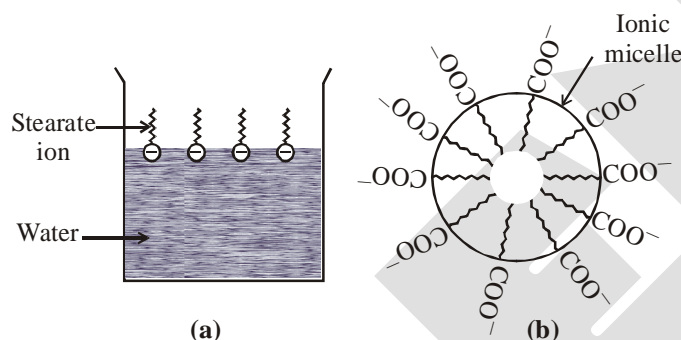
Let us take the example of soap solutions. Soap is sodium or potassium salt of a higher fatty acid and may be represented as  $\text{RCOO}^-\text{Na}^+$  (e.g., sodium stearate  $\text{CH}_3(\text{CH}_2)_{16}\text{COO}^-\text{Na}^+$ , which is a major component of many bar soaps). When dissolved in water, it dissociates into  $\text{RCOO}^-$  and  $\text{Na}^+$  ions. The  $\text{RCOO}^-$  ions, however, consist of two parts — a long hydrocarbon chain R (also called non-polar 'tail') which is hydrophobic (water repelling), and a polar group  $\text{COO}^-$  (also called polar-ionic 'head'), which is hydrophilic (water loving).





The  $\text{RCOO}^-$  ions are, therefore, present on the surface with their  $\text{COO}^-$  groups in water and the hydrocarbon chains  $\text{R}$  staying away from it and remain at the surface. But at critical micelle concentration, the anions are pulled into the bulk of the solution and aggregate to form a spherical shape with their hydrocarbon chains pointing towards the centre of the sphere with  $\text{COO}^-$  part remaining outward on the surface of the sphere. An aggregate thus formed is known as 'ionic micelle'. These micelles may contain as many as 100 such ions.

Similarly, in case of detergents, e.g., sodium laurylsulphate,  $\text{CH}_3(\text{CH}_2)_{11}\text{SO}_4^- \text{Na}^+$ , the polar group is  $-\text{SO}_4^-$  along with the long hydrocarbon chain. Hence, the mechanism of micelle formation here also is same as that of soaps.

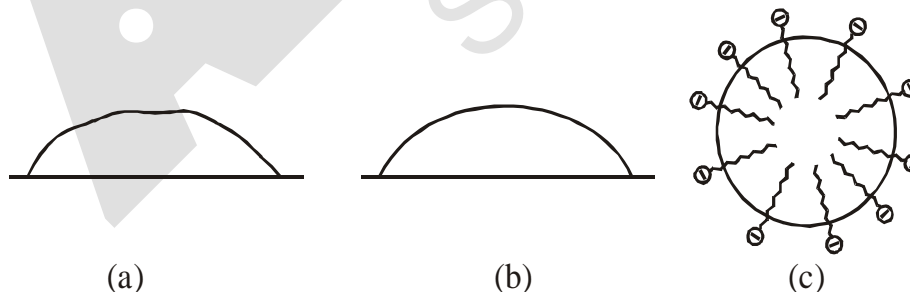


(a) Arrangement of stearate ions on the surface of water at low concentration of soap

(b) Arrangement of stearate ions inside the bulk of water (ionic micelle) at critical micelle concentration of soap

### Cleansing action of soaps :

It has been mentioned earlier that a micelle consists of a hydrophobic hydrocarbon – like central core. The cleansing action of soap is due to the fact that soap molecules form micelle around the oil droplet in such a way that hydrophobic part of the stearate ions is in the oil droplet and hydrophilic part projects out of the grease droplet like the bristles. Since the polar groups can interact with water, the oil droplet surrounded by stearate ions is now pulled in water and removed from the dirty surface. The negatively charged sheath around the globules prevents them from coming together and forming aggregates.



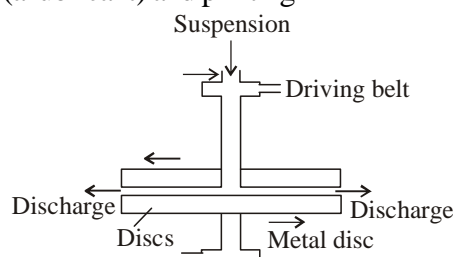
(a) Grease on cloth (b) Stearate ions arranging around the grease droplet and  
(c) Grease droplet surrounded by stearate ions (micelle formed)

**LIST OF SURFACTANTS AND THEIR CRITICAL MICELLE CONCENTRATION (CMC)**

| Surfactant                                                                     | CMC (g/l)            | Temp.(°C) |
|--------------------------------------------------------------------------------|----------------------|-----------|
| <b>Anionic</b>                                                                 |                      |           |
| $\text{CH}_3(\text{CH}_2)_6\text{COONa}$                                       | $6.5 \times 10^1$    | 20        |
| $\text{CH}_3(\text{CH}_2)_{10}\text{COONa}$                                    | 5.6                  | 20–70     |
| $\text{CH}_3(\text{CH}_2)_7\text{OSO}_3\text{Na}$                              | $3.0 \times 10^1$    | 25–50     |
| $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$                           | 2.6                  | 25–60     |
| $\text{CH}_3(\text{CH}_2)_5\text{C}_6\text{H}_4\text{SO}_3\text{Na}$           | 9.8                  | 75        |
| $\text{CH}_3(\text{CH}_2)_{11}\text{C}_6\text{H}_4\text{SO}_3\text{Na}$        | $4.0 \times 10^{-1}$ | 50–75     |
| <b>Cationic</b>                                                                |                      |           |
| $\text{CH}_3(\text{CH}_2)_9\text{NH}_2\cdot\text{HCl}$                         | 8.5                  | 25        |
| $\text{CH}_3(\text{CH}_2)_{11}\text{NH}_2\text{HCl}$                           | 2.7                  | 30–50     |
| $\text{CH}_3(\text{CH}_2)_7\text{N}(\text{CH}_3)_3\text{Br}$                   | $7.8 \times 10^1$    | 25        |
| $\text{CH}_3(\text{CH}_2)_{11}\text{N}(\text{CH}_3)_3\text{Br}$                | 5.4                  | 25        |
| <b>Non-ionic</b>                                                               |                      |           |
| $\text{CH}_3(\text{CH}_2)_7\text{C}_6\text{H}_{11}\text{O}_6$                  | 7.3                  | 25        |
| $\text{C}_{12}\text{H}_{20}\text{O}_9(\text{C}_{16}\text{H}_{31}\text{O}_2)_2$ | $1.1 \times 10^{-2}$ | 20        |
| $\text{CH}_3(\text{CH}_2)_{10}\text{COOC}_{12}\text{H}_{21}\text{O}_{10}$      | $7.1 \times 10^{-3}$ | 50        |

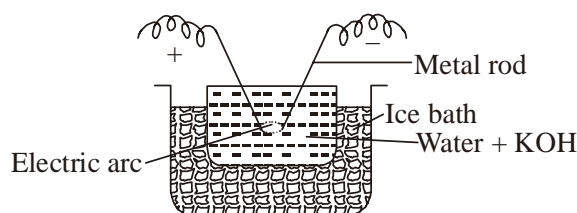
**4.4 PREPARATION OF COLLOIDAL SOLUTIONS :**

- (1) **Preparation of lyophilic sols :** The colloidal solutions of lyophilic colloids like starch, glue, gelatin etc., can be readily prepared by dissolving these substances in water either by cooling or warming. Solutions of colloidal electrolytes such as soaps and dye stuffs can also be prepared similarly.
  - (2) **Preparation of lyophobic sols :** To get a substance in colloidal form either the substance in bulk is broken down into fine particles of colloidal dimension ( $1\text{Å}$  to  $10^3\text{Å}$ ) or increasing the size of molecular particles as to form larger aggregates. In some cases, a third substance is added to increase the stability of the sol. These substances are called stabilizers. Thus, there are two ways by which the lyophobic sols can be prepared :
    - (i) **Dispersion methods :** By splitting coarse aggregates of a substance into colloidal size.
    - (ii) **Condensation methods :** By aggregating very small particles (atoms, ions or molecules) into colloidal size.
- (i) Dispersion Methods :**
- (A) **Mechanical dispersion :** Solid material is first finely ground by usual methods. It is then mixed with dispersion medium which gives a coarse suspension. The suspension is now introduced into the colloid mill. The simplest form of colloid mill consists of two metal discs held at a small distance apart from one another and capable of revolving at a very high speed (about 7000 revolutions per minute) in opposite directions. The particles are ground down to colloidal size and are then dispersed in the liquid. A stabilizer is often added to stabilize the colloidal solution. Colloidal graphite (a lubricant) and printing ink



are made by this method. Tannin is used as a stabilizer in the preparation of colloidal graphite and gum arabic in lampblack colloidal solution (Indian ink).

- (B) **Electro-dispersion (Bredig's arc method)** : This method is suitable for the preparation of colloidal solutions of metals like gold, silver, platinum, etc. An arc is struck between the metal electrodes under the surface of water



container in an ice bath. The intense heat of the arc vaporises some of the metal which condenses under cold water.

- (C) **Ultrasonic dispersion** : The sound waves of high frequency are usually called ultrasonic waves. These waves can be produced when quartz crystal discs are connected with a high frequency generator. The application of ultrasonic waves for the preparation of colloidal solutions was first introduced by Wood and Loomis, in 1927. Various substances like oils, mercury, sulphur, sulphides and oxides of metals can be dispersed into colloidal state very easily with the help of ultrasonic waves.
- (D) **Peptization** : Peptization may be defined as the process of converting a precipitate into colloidal sol by shaking it with dispersion medium in the presence of a small amount of electrolyte. The electrolyte used for this purpose is called peptizing agent. This method is applied, generally, to convert a freshly prepared precipitate into a colloidal sol. During peptization, the precipitate adsorbs one of the ions of the electrolyte on its surface. This causes the development of positive or negative charge on precipitates, which ultimately break up into smaller particles of the size of a colloid.

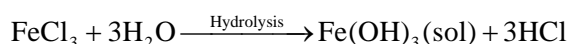
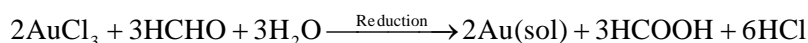
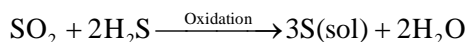
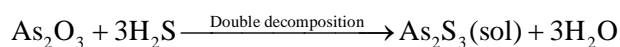
A few examples of sols obtained by peptization are :

- (i) Freshly prepared ferric hydroxide on treatment with a small amount of ferric chloride solution at once forms a dark reddish brown solution. Ferric chloride acts as a peptizing agent.
- (ii) Freshly precipitated silver chloride can be converted into a colloidal solution by a small amount of hydrochloric acid.
- (iii) Cadmium sulphide can be peptized with the help of hydrogen sulphide.

(ii) **Condensation Methods :**

- (A) **By exchange of solvents** : If a solution of sulphur or phosphorus prepared in alcohol is poured into water, a colloidal solution of sulphur or phosphorus is obtained due to low solubility of sulphur or phosphorus in water. Thus, there are a number of substances whose colloidal solutions can be prepared by taking a solution of the substance in one solvent and pouring it into another solvent in which the substance is relatively less soluble.
- (B) **By change of physical state** : Colloidal solutions of certain elements such as mercury and sulphur are obtained by passing their vapour through cold water containing a stabilizer (an ammonium salt or a citrate)

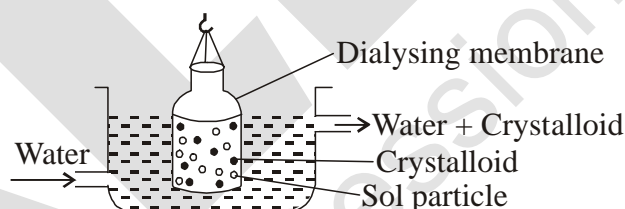
- (C) **Chemical methods** : Colloidal solutions can be prepared by chemical reactions leading to formation of molecules by double decomposition, oxidation, reduction or hydrolysis. These molecules then aggregate leading to formation of sols.



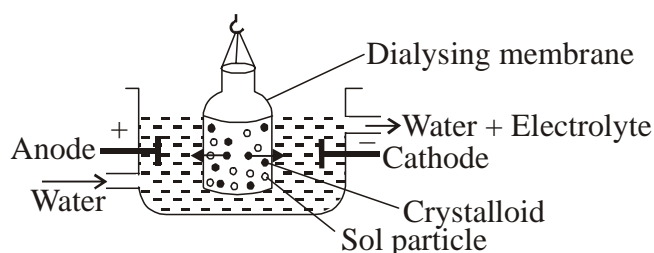
#### 4.5 PURIFICATION OF COLLOIDAL SOLUTIONS :

Colloidal solutions prepared by above methods generally contain excessive amount of electrolytes and some other soluble impurities. The presence of traces of electrolyte is essential for the stability of the colloidal solution but larger quantities coagulate it. It is, therefore, necessary to reduce the concentration of these soluble impurities to a requisite minimum. The process used for reducing of these impurities to a requisite minimum is known as purification of colloidal solution. The purification of colloidal solution is carried out by the following methods.

- (i) **Dialysis** : It is a process of removing a dissolved substance from a colloidal solution by means of diffusion through suitable membrane. Since, particles in true solution (ions or smaller molecules) can pass through animal membranes (bladder) or parchment paper or cellophane sheet but colloidal particles do not, the above can be used for dialysis. The apparatus used for this purpose is called **dialyser**. A bag of suitable membrane containing the colloidal solution is suspended in a vessel through which fresh water is continuously flown figure. The dissolved substances and ions diffuse through the membrane into the outer water and pure colloidal solution is left behind.



- (ii) **Electro-dialysis** : Ordinarily, the process of dialysis is quite slow. It can be made faster by applying an electric field if the dissolved substance in the impure colloidal solution is only electrolyte. The process is then named electro-dialysis. The colloidal solution is placed between two electrodes while pure water is taken in a compartment on each side. Electrodes are fitted in the compartment as shown in figure the ions present in the colloidal solution migrate out to the oppositely charged electrodes.



- (iii) **Ultrafiltration** : Ultrafiltration is the process of separating the colloidal particles from the solvent and soluble solutes present in the colloidal solution by especially prepared filters, which are permeable to all substances except the colloidal particles.

Colloidal particles can pass through ordinary filter paper because the pores are too large. However, the pores of filter paper can be reduced in size by impregnating with collodion solution and subsequently hardened by soaking in formaldehyde. The usual collodion is a 4% solution of nitro-cellulose in a mixture of alcohol and ether. An ultrafilter paper may be prepared by soaking the filter paper in a collodion solution and hardened by formaldehyde and finally drying it. Thus, by using ultrafilter paper, the colloidal particles are separated from rest of the materials. Ultrafiltration is a slow process. To speed up the process, pressure or suction is used.

The colloidal particles left on the ultrafilter paper are then stirred with fresh dispersion medium (solvent) to get a pure colloidal solution.

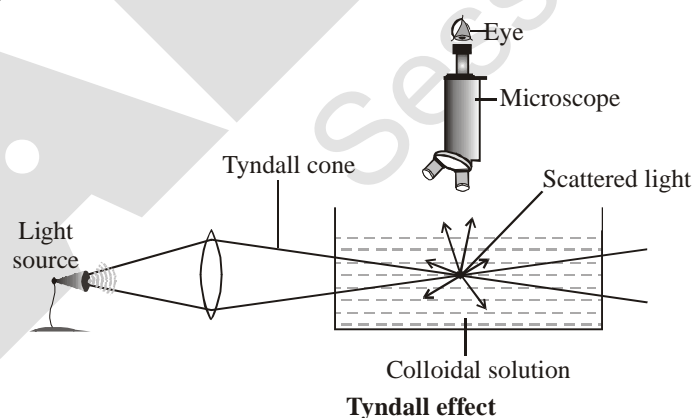
## 4.6 PROPERTIES OF COLLOIDAL SOLUTIONS :

### 4.6.1 Colligative properties:

Colloidal particles being bigger aggregates, the number of particles in a colloidal solution is comparatively small as compared to a true solution. Hence, the values of colligative properties (osmotic pressure, lowering in vapour pressure, depression in freezing point and elevation in boiling point) are of small order as compared to values shown by true solutions at same concentrations.

### 4.6.2 Optical Properties :

- (I) **Tyndal Effect** : When a strong and converging beam of light is passed through a colloidal solution, its path becomes visible (bluish light) when viewed at right angles to the beam of light. This effect is called **Tyndall effect**. The light is observed as a bluish cone which is called **Tyndall cone**. The Tyndall effect is due to scattering of light by the colloidal particles. The scattering of light cannot be due to simple reflection, because the size of the particles is smaller than the wave, length of the visible light and they are unable to reflect light waves. In fact, colloidal particles first absorb light and then a part of the absorbed light is scattered from the surface of the colloidal particles as a light of shorter wavelength. Since maximum scattering of light takes place at right angles to the place of incident light, it becomes visible when seen from that direction.



**Tyndall effect**

The Tyndall effect is observed under the following conditions :

- The diameter of the dispersed particles must not be much smaller than the wavelength of light employed.
  - The refractive indices of the dispersed phase and the dispersion medium must differ widely. This condition is fulfilled by lyophobic colloids.
- It is important to note that Tyndall effect is not shown by true solutions as their particles are too small to cause scattering.

**Note :**

Tyndall effect is used to distinguish between a colloidal and true solution. Zsigmondy, in 1903, used Tyndall effect to set up an apparatus known as ultramicroscope. An intense beam of light is focussed on the colloidal solution contained in a glass vessel. The focus of the light is then observed with a microscope at right angles to the beam. Individual colloidal particles appear as bright stars against a dark background. Ultramicroscope does not render the actual colloidal particles visible but only observe the light scattered by them. Thus, ultramicroscope does not provide any information about the size and shape of colloidal particles.

(II) **Colour :** The colour of the colloidal solution is not always the same as the colour of the substances in the bulk. The colour of the colloidal solution depends upon the following factors :

- Size and shape of colloidal particles.
- Wavelength of the light scattered by dispersed particles.
- The way an observer receives the light, i.e., whether by reflection or by transmission.

**Examples :**

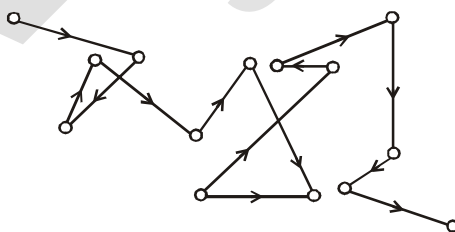
- Finest gold is red in colour. As the size of particles increases, it appears purple, then blue and finally golden.
- Dilute milk gives a bluish tinge in reflected light whereas reddish tinge in transmitted light.

**4.6.3 Mechanical Properties :**

(a) **Brownian movement :** Colloids particles exhibit a ceaseless random and swarming motion. This kinetic activity of particles suspended in the liquid is called Brownina movement.

Robert Brown a British Botanist first observed this motion with pollen grains suspended in water.

**Cause of movement :** The Brownian movement has been explained to be due to the unbalanced bombardment of the particles by the molecules of the dispersion medium. The Brownian movement has a stirring effect which does not permit the particles to settle and thus, is responsible for the stability of sols.



**Brownian movement**

**Importance :**

Brownian movement does not allow the colloidal particles to settle down due to gravity and thus is responsible for their stability.



## 4.6.4 Electrical Properties :

## (I) Charge of colloidal particles :

**Origin of charge :** Various reasons have been given regarding the original of charge on the colloidal particles. These are given below :

- (i) **Frictional electrification :** It is believed to be frictional due to the rubbing of the dispersed phase particles with medium molecules.
- (ii) **Dissociation of the surface molecules :** It leads to electric charge on colloidal particles. For example, an aqueous solution of a soap (sodium palmitate) dissociates into ions.  

$$\text{C}_{15}\text{H}_{31}\text{COONa} \rightleftharpoons \text{C}_{15}\text{H}_{31}\text{COO}^- + \text{Na}^+$$
 sod. palmitate  
 The  $\text{Na}^+$  ions pass into the solution while  $\text{C}_{15}\text{H}_{31}\text{COO}^-$  ions have a tendency to form aggregates due to weak attractive forces present in the hydrocarbon chains. Thus, the anions which are of colloidal size bear negative charge.
- (iii) **Preferential adsorption of ions from solution :** The charge on the colloidal particles is generally acquired by preferentially adsorbing positive or negative ions from the electrolyte. Thus  $\text{AgCl}$  particles can adsorb  $\text{Cl}^-$  ions from chloride solutions and  $\text{Ag}^+$  ions from excess  $\text{Ag}^+$  ions solutions; the sol. will be negatively charged in the first case and positively charged in the second case.
- (iv) **Capture of electron :** It is from air during preparation of sol. by Bredig's arc method.
- (v) **Dissociation of molecular electrolytes on the surface of particles :**  $\text{H}_2\text{S}$  molecules get adsorbed on sulphides during precipitation. By dissociation of  $\text{H}_2\text{S}$ ,  $\text{H}^+$  ions are lost and colloidal particles become negatively charged.

Colloidal particles always carry an electric charge. The nature of this charge is the same on all the particles in a given colloidal solution and may be either positive or negative. A list of some common sols with the nature of charge on their particles is given below:

| Positively charged sols                                                                                                                                                                  | Negatively charged sols                                                                         |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------|
| Hydrated metallic oxides, e.g. $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ , $\text{CrO}_3 \cdot x\text{H}_2\text{O}$ and $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ , etc. | Metals, e.g. copper, silver, gold sols.                                                         |
| Basic dye stuffs, e.g., methylene blue sol.                                                                                                                                              | Metallic sulphide, e.g., $\text{As}_2\text{S}_3$ , $\text{Sb}_2\text{S}_3$ , $\text{CdS}$ sols. |
| Haemoglobin (blood)                                                                                                                                                                      | Acid dye stuffs, e.g. eosin congo red sols.                                                     |
| Oxides, e.g. $\text{TiO}_2$ sol.                                                                                                                                                         | Sols of starch, gum, gelatin, clay, charcoal, etc.                                              |

The charge on the sol particles is due to one or more reasons, viz., due to electron capture by sol particles during electrodispersion of metals, due to preferential adsorption of ions from solution and/or due to formulation of electrical double layer. Preferential adsorption of ions is the most accepted reason. The sol particles acquire positive or negative charge by preferential adsorption of positive or negative ions. When two or more ions are present in the dispersion medium, preferential adsorption of the ion common to the colloidal particle usually takes place. This can be explained by taking the following examples:

- (a) When silver nitrate solution is added to potassium iodide solution, the precipitated silver iodide adsorbs iodide ions from the dispersion medium and negatively charged colloidal solution results. However, when KI solution is added to  $\text{AgNO}_3$  solution, positively charged sol results due to adsorption of  $\text{Ag}^+$  ions from dispersion medium.

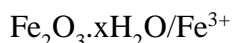


Negatively charged



Positively Charged

- (b) If  $\text{FeCl}_3$  is added to excess of hot water, a positively charged sol of hydrated ferric oxide is formed due to adsorption of  $\text{Fe}^{3+}$  ions. However, when ferric chloride is added to  $\text{NaOH}$  a negatively charged sol is obtained with adsorption of  $\text{OH}^-$  ions.

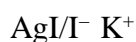


Positively charged

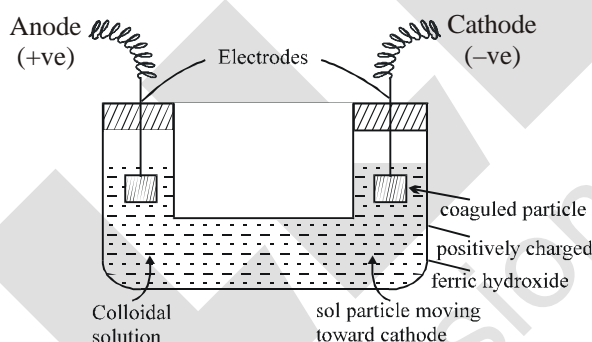


Negatively charged

Having acquired a positive or a negative charge by selective adsorption on the surface of a colloidal particle as stated above, this layer attracts counter ions from the medium forming a second layer, as shown below.



- (II) **Electrophoresis** : In a colloidal solution, the colloidal particles are electrically charged and the dispersion medium has equal but opposite charge. Thus colloidal solution on the whole is electrically neutral. When an electric current is passed through a colloidal solution, the charged particles move towards the oppositely charged electrode where coagulate due to loss of charge.



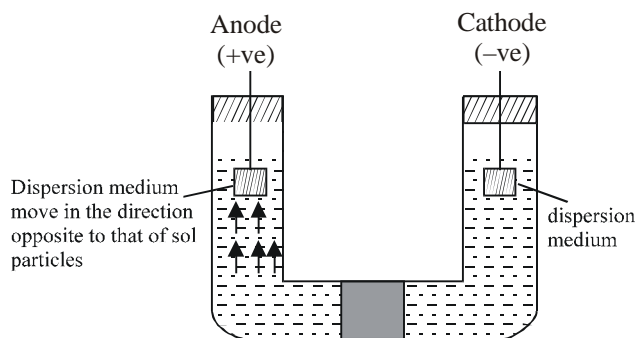
The phenomenon involving the migration of colloidal particles under the influence of electric field towards the oppositely charged electrode, is called electrophoresis or cataphoresis.

This phenomenon is used to determine the charge on the colloidal particles. For example, when a sol. of ferric hydroxide is taken in a U-tube and subjected to electric field, the ferric hydroxide (sol.) particles get accumulated near the cathode. This shows that ferric hydroxide sol. particles are positively charged.

- (III) **Electro-osmosis** : The phenomenon involving the migration of the dispersion medium and not the colloidal particles under the influence of an electric field is electro-osmosis.

Take the pure solvent (dispersion medium) in two limbs of U-tube. In the lower middle portion of U-tube, a porous diaphragm containing the colloidal system is present which divides the U-tube in two sections. In each section of U-tube, an electrode is present, as shown in figure. When the electrode potential is applied to the electrodes, the solid phase of sol. (colloidal system) cannot move but the solvent (dispersion medium) moves through the porous diaphragm towards one of the electrodes. The direction of migration of dispersion medium due to electro-osmosis determines the charge on sol. particles e.g., if the dispersion medium moves towards the cathode (negative electrode), the sol. particles are also negatively charged because the dispersion medium is positively charged as on the whole colloidal solution is neutral.





(IV) **Zeta potential,  $\xi$**  : The combination of the two layers of opposite charges around the colloidal particle is called **Helmholtz electrical double layer**. According to modern views, the first layer of ions is firmly held and is termed **fixed layer** while the second layer is mobile which is termed **diffused layer**. Since separation of charge is a seat of potential, the charges of opposite signs on the fixed and diffused parts of the double layer results in a difference in potential between these layers. This potential difference between the fixed layer and the diffused layer of opposite charges is called the **electrokinetic potential or zeta potential**. The presence of equal and similar charges on colloidal particles is largely responsible in providing stability to the colloidal solution, because the repulsive forces between charged particles having same charge prevent them from coalescing or aggregating when they come closer to one another.

(V) **Isoelectric point** : It is the pH at which the colloidal particles do not carry any charge.

#### 4.7 COAGULATION :

The colloidal sols are stable due to the presence of electric charges on the colloidal particles. Because of the electrical repulsion, the particles do not come close to one another to form precipitates. The removal of charge by any means will lead to the aggregation of particles and hence precipitation will occur immediately.

**This process by means of which the particles of the dispersed phase in a sol. are precipitated is known as coagulation.**

If the coagulated particles instead of settling at the bottom of the container, float on the surface of the dispersion medium, the coagulation is called flocculation.

Most of the sols are coagulated by adding an electrolyte of opposite sign. This is due to the fact that the colloidal particles take up the ions of electrolyte whose charges are opposite to that on colloidal particles with the result that charge on the colloidal particles is neutralized. Thus coagulation takes place. For example, arsenious sulphide sol. (negatively charged) precipitated by adding barium chloride solution. It is due to the fact that the negatively charged particles of the sol. take up barium ions and get neutralized which lower the stability. As a result coagulation takes place.

It is observed that different amounts of different electrolytes is required to bring coagulation of a particular solution.

The minimum concentration of an electrolyte in millimoles per litre required to cause precipitation of one litre of a colloidal solution in two hours is called (**coagulation in value or flocculation value**) of the electrolyte for the sol. The smaller the quantity needed the higher will be the coagulating power of an ion. The reciprocal of coagulation value is regarded as the coagulating power the

For example, the coagulation values of NaCl, BaCl<sub>2</sub> and AlCl<sub>3</sub> for arsenic sulphide sol. are 51, 0.69 and 0.093 millimoles/litre respectively. Thus their coagulating powers are  $\frac{1}{51}$ ,  $\frac{1}{0.69}$  and  $\frac{1}{0.093}$  i.e., 0.0196, 1.449 and 10.75 respectively.

The coagulation values of a few electrolytes for negatively charged arsenic sulphide and positively charged ferric hydroxide sol. are given in table given below. The valency of the coagulation ion (the ion whose charge is opposite to that of the colloidal particles) is also given.

**Coagulation values of different electrolytes**

| Arsenic sulphide sol.          |                   |                   | Ferric hydroxide sol.              |                  |                   |
|--------------------------------|-------------------|-------------------|------------------------------------|------------------|-------------------|
| Electrolyte coagulating cation | Valency of cation | coagulation value | Electrolyte coagulating            | Valency of anion | coagulation value |
| K <sub>2</sub> SO <sub>4</sub> | 1                 | 63                | KBr                                | 1                | 138               |
| NaCl                           | 1                 | 51                | KNO <sub>3</sub>                   | 1                | 132               |
| KNO <sub>3</sub>               | 1                 | 50                | KCl                                | 1                | 103               |
| MgSO <sub>4</sub>              | 2                 | 0.81              | K <sub>2</sub> CrO <sub>4</sub>    | 2                | 0.320             |
| BaCl <sub>2</sub>              | 2                 | 0.69              | K <sub>2</sub> SO <sub>4</sub>     | 2                | 0.215             |
| AlCl <sub>3</sub>              | 3                 | 0.093             | K <sub>3</sub> Fe(CN) <sub>6</sub> | 3                | 0.096             |

From the above table, it is clear that the coagulating power of Al<sup>3+</sup> ions in precipitating the arsenic sulphide sol. is approximately 550 times more than that of sodium (Na<sup>+</sup>) or potassium (K<sup>+</sup>) ions. Again, it is observed that the negatively charged arsenic sulphide sol. is coagulated by cations while positively charged ferric hydroxide sol. is coagulated by anions.

**Hardy-Schulz rules :** H. Schulze (1882) and W.B. Hardy (1900) suggested the following rules to discuss the effect of electrolytes of the coagulation of the sol.

- (1) Only the ions carrying charge opposite to the one present on the sol. particles are effective to cause coagulation, e.g., the negative charged sol. is best coagulated by cations and a positive sol. is coagulated by anions.
- (2) The charge on coagulating ion influences the coagulation of sol.

In general, the coagulating power of the active ion increases with the valency of the active ion. After observing the regularities concerning the valency of the active ion, a law was proposed by Hardy and Schulz which is termed as Hardy-Schulze law which is stated as follows: "Higher is the valency of the active ion, greater will be its power to precipitate the sol."

Thus, coagulating power of cations is in the order of Al<sup>3+</sup> > Ba<sup>2+</sup> or Mg<sup>2+</sup> > Na<sup>+</sup> or K<sup>+</sup>.

Similarly, to coagulating the positively charged sol. the coagulating power of anion is in the order of [Fe(CN)<sub>6</sub>]<sup>4-</sup> > PO<sub>4</sub><sup>3-</sup> > SO<sub>4</sub><sup>2-</sup> > Cl<sup>-</sup>

**Ex3.** 11.7 gm NaCl is needed for complete coagulation on 50 l of a colloidal solution. What is the coagulation value of electrolyte ?

$$\text{Sol. Coagulation value} = \frac{\text{millimole of electrolyte}}{\text{L of colloidal solution}} = \frac{\frac{11.7}{58.5} \times 1000}{50} = 4$$

#### Some other methods of coagulation :

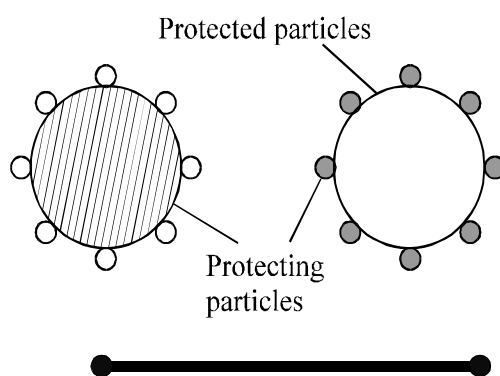
Apart from the addition of electrolyte, coagulation can also be carried out by following methods:

- (i) **By persistent dialysis :** It has been observed that traces of electrolytes are associated with the solution due to which it is stable. If the solution is subjected to prolonged dialysis, the traces of electrolytes are removed and coagulation takes place.
- (ii) **By mutual coagulation of colloids :** When two sols of oppositely charges are mixed together in a suitable proportion, the coagulation takes place. The charge of one is neutralized by the other. For example, when negatively charged arsenic sulphide sol. is added to positively charged ferric hydroxide sol., the precipitation of both occurs simultaneously.
- (iii) **By electrical method :** If the electrical charge of lyophobic sol. is removed by applying any electric field such as in electrophoresis, they also precipitate out.
- (iv) **By boiling:** When a sol is boiled, the adsorbed layer is disturbed due to increased collisions with the molecules of dispersion medium. This reduces the charge on the particles and ultimately lead to settling down in the form of a precipitate.
- (v) **By addition of electrolytes:** When excess of an electrolyte is added, the colloidal particles are precipitated. The reason is that colloids interact with ions carrying charge opposite to that present on themselves. This causes neutralisation leading to their coagulation. The ion responsible for neutralisation of charge on the particles is called the coagulating ion. A negative ion causes the precipitation of positively charged sol and vice versa.

#### 4.8 PROTECTIVE COLLOIDS :

Lyophilic sols are more stable than the lyophobic sols. This is because, lyophilic colloids are extensively hydrated and these hydrated particles do not combine to form large aggregates.

Lyophobic sols are more easily coagulated by the addition of suitable electrolyte. To avoid the precipitation of lyophobic sol, by the addition of electrolyte, some lyophilic colloid is added to it. Such lyophilic colloid is called protective colloid and the protection of lyophobic colloid from the electrolytes is known as **protection**. The substances commonly used as protective colloids are gelatin, albumin, gum arabic, casein, starch, glue etc. A gold sol. containing a little gelatin as protective colloid needs a very large amount of sodium chloride to coagulate the sol.



**Explanation :** The particles of the protective colloid get adsorbed on the particles of the lyophobic colloid, thereby forming a protective layer around it (figure). The protective layer prevents the precipitating ions from coming in contact with the colloidal particles.

According to a recent view, the increase in stability of the lyophobic colloid is due to the mutual adsorption of the lyophilic and lyophobic colloids. It is immaterial which is adsorbed on which.

**Gold number of a protective colloid is a minimum weight of it in milligrams which must be added to 10 ml of a standard red gold sol so that no coagulation of the gold sol. (i.e. change of colour from red to blue) takes place when 1 ml of 10 % sodium chloride solution is rapidly added to it. Obviously, smaller the gold number of a protective colloid, the greater is the protective action.**

**Ex.4** 0.02 gm of lyophilic colloid just present coagulation in 10 ml of a lyophobic colloid on adding 1 ml of 10 % NaCl solution. What is the gold number of lyophilic colloid ?

**Sol.** Mg of lyophilic colloid =  $0.02 \times 1000 = 20$

#### 4.9 EMULSIONS :

An emulsion is a colloidal solution of a liquid. It may be defined as a heterogeneous system consisting of more than one immiscible liquids dispersed in one another in the form of droplets

For example, milk is an emulsion in which small drops of liquid fat are dispersed in aqueous medium.

Cod liver oil is an emulsion in which the water drops are dispersed in the oil. This means in most of the emulsions one of the liquid is water and the other liquid in oil.

The emulsion are classified as :

- (1) **Oil in water type emulsion (O/W):** In this emulsion, oil is the dispersed phase and water is the dispersion medium. It is denoted by O/W or O in W. For example, milk (liquid fat dispersed in water), vanishing cream.
- (2) **Water in oil type :** In this emulsion, water is the dispersed phase and oil is the dispersion medium. It is denoted by W/O or W in O. For example, butter.

The type of emulsion obtained by agitating two immiscible liquids depends upon the relative amounts of two components liquids. The liquid that is in excess forms the dispersion medium. Thus, the two types of emulsions can be interconverted into each other by changing the concentration of one of the liquids.

**4.9.1 Preparation of emulsion (Emulsification) :** Emulsification is the process which involves the preparation of emulsion. Generally, an emulsion is prepared by subjecting a mixture of the immiscible liquid to a distinct layers upon standing. The oil globules rise to form an upper layer while aqueous medium forms lower layers. To prevent the separation of layers and to get the stable emulsion, a small quantity of the third substance is added. This substance which stabilizes the emulsion is called emulsifier or emulsifying agent. The commonly used emulsifying agents are soaps, detergents and lyophilic colloids. Casein, a lyophilic colloid present in milk, acts as an emulsifier as it forms a protective layer around fat molecules dispersed in water. Hence milk is a fairly stable emulsion.

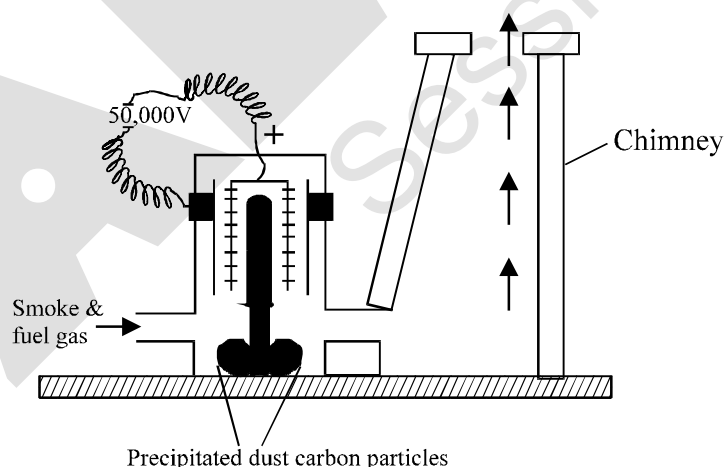
**Function of emulsifier :** The main function of emulsifier or emulsifying agents is to lower the interfacial tension between oil and water and thus helps the intermixing of two liquids. For example, a molecule of a soap or detergent (emulsifier) gets concentrated at the interface between oil and water. The polar end of the emulsifier is in water and non-polar end is in oil as shown in figure.

In a soap,  $\text{RCOONa}$ , R is the non-polar end, whereas  $\text{COO}^- \text{Na}^+$  is the polar end.



## 4.10 USES OF COLLOIDS :

- (1) **Medicines** : The medicines containing gold, silver or calcium etc. in colloidal form are more effective and easily assimilated by the human systems.
- (2) **Dyes** : In dyeing, mordants colloidal substances are used in textile dyeing industry to fasten dyes.
- (3) **Rubber industry** : Latex is a colloidal solution of negatively charged particles. The article to be rubber plated is made the anode. Under the influence of electric field the rubber particles get deposited on the anode and the article gets rubber plated.
- (4) **Smoke screens** : Smoke screens which consist of titanium dioxide dispersed in air are used in warfare for the purpose of concealment and camouflage.
- (5) **Formation of delta** : The river water carries with it charged clay particles and many other substances in the form of colloidal solution. When the sea water comes in contact with these particles, the colloidal particles in river water are coagulated by the electrolytes present in sea water to form deltas.
- (6) **Purification of water** : The turbidity in water is due to the presence of negatively charged clay particles. The addition of potash alum, i.e.,  $\text{Al}^{3+}$  ions neutralizes the negative charge on the colloidal particles and thus causes their coagulation. The coagulated matter settles down and thus becomes clear.
- (7) **Artificial rain** : Artificial rain can be caused by throwing electrified sand on clouds which are colloidal solutions or charged particles of water in air.
- (8) **Smoke precipitation** : Smoke coming out of the chimney is industrial area is a nuisance and health hazard. It is a colloidal particles are charged particles and thus they are removed from fuel gases by electrical precipitation (Cottrell Precipitator).

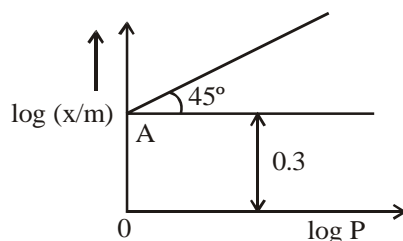


In cottrell precipitator, the smoke is made to pass through chambers fitted with highly electrically charged plates which precipitate the carbon and dust particles leaving in the gases to escape through chimney (figure).

- (9) **Sewage disposal :** Sewage water consists of particles of dirt, rubbish, mud, etc., which are of colloidal dimensions and carry an electric charge and thus do not settle down easily. These particles can thus be removed by cataphoresis. A system of two tanks fitted with metallic electrodes is used for this purpose. When electric field is created, then the dust particles are coagulated on the oppositely charged electrodes. The deposit may be utilized as a manure.
- (10) **Cleansing action of soap and detergent :** Soap solution may be used to wash off the dirt sticking to the fabric, in the presence
- If forms a colloidal solution in water forms (miscelles), removes dirt by simple adsorption of oily substance and thus washes away.
  - It decreases the interfacial tension between water and grease, and it causes the emulsification of grease in water. By mechanical action such as rubbing, the dirt particles are also detached along with the oily material.
- (11) **In Photography :** Various colloidal systems are used in photographic process. In the preparation of photographic plates, the silver bromide in gelatin is coated on thin glass plates. In developing and fixation, various colloidal substances are used. In different kinds of colour printing, gelatin and other colloidal mixtures are used.
- (12) **Blue colour of the sky :** Colloidal particles scatter only blue light and the rest of it is absorbed. In sky there are a number of dust and water particles. They scatter blue light and, therefore, sky looks bluish. If there were no scattering, the sky would have appeared totally dark.

## EXERCISE # S-1

1. Graph between  $\log \left( \frac{x}{m} \right)$  vs  $\log P$  is provided for adsorption of  $\text{NH}_3$  gas on metal surface. Calculate weight of  $\text{NH}_3$  gas adsorbed by 50 gm of metal surface at 2 atm pressure



2. When a graph is plotted between  $\log x/m$  and  $\log P$  (where  $P$  is in atm), it is straight line with an angle of  $45^\circ$  and intercept 0.3010 on y-axis, what will be the amount of gas adsorbed per gm of adsorbent at pressure 0.3 atm ( $\log 2 = 0.3010$ )
3. In vessel  $\text{O}_2$  gas undergoes physisorption on adsorbent surface causing its partial pressure to decrease from 6 atm to ' $P$ ' atm in a 8.21 L vessel at 500K. If total number of sites is  $2 \times 10^{23}$  on adsorbent surface and every site accommodates effectively three  $\text{O}_2$  molecules find  $P(\text{atm})$ .  
[ $N_A = 6 \times 10^{23}$ ]
4. 1.25 mg of Gum Arabica (Gold Number = 0.25) is added to 50 ml of standard gold sol. What maximum volume (in ml) of 10% NaCl solution can be added to this gold sol without causing coagulation.
5. Gold number of haemoglobin is 0.3. Calculate weight (in mg) of haemoglobin for 100 ml of gold sol so that gold sol is not coagulated by 10 ml of 10% NaCl solution.
6. A soap ( $\text{C}_{17}\text{H}_{35}\text{COONa}$ ) solution becomes a colloidal sol at a concentration of  $1.2 \times 10^{-3}$  M. On the average,  $2.4 \times 10^{13}$  colloidal particles are present in  $1 \text{ mm}^3$ . What is the average number of stearate ions in one colloidal particle (micelle) : **Take : Avogadro's number =  $6 \times 10^{23}$**
7. How many of the following phenomenon are observed due to process of coagulation.
- (A) Delta formation at the meeting point of river and sea.
  - (B) Blue colour of sky.
  - (C) Precipitation of coal ash from smoke in chimeney's.
  - (D) destruction of lyophobic solution.
  - (E) Brownian motion.
  - (F) Cleaning action of detergents.
  - (G) Artificial rain.
  - (H) Use of alums in cleaning water.



8. Calculate the number of sols which are negatively charged.

$\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$  sol

$\text{Sb}_2\text{S}_3$  sol

Ag sol

Cu sol

Blood

basic dye

sol of clay

sol of starch

sol of sodium stearate

sol of sodium laurylsulphate

sol of charcoal.

9. In order to cause coagulation of 200 ml of gold sol, 585 ml of 1% w/w NaCl solution having density 1.2 gm/ml was required. What will be the coagulation value of NaCl?

[express answer in milli-moles /litre]

10. Molecular formula of starch can be represented as  $(\text{C}_6\text{H}_{10}\text{O}_5)_n$ . If the gold number of one such starch molecule is 6.48 and 0.01 millimoles of the above starch are required to be added to 10ml of gold sol to prevent coagulation by 1 ml of 10% sodium chloride solution, then calculate the value of 'n'.

EXERCISE # S-2

- In a vessel  $O_2$  gas molecules were adsorbed on solid surface causing its partial pressure to decrease from 1 atm to 0.5 atm.  
**Given :**  $N_A = 6 \times 10^{23}$   
 Volume of vessel = 2.24 L  
 Temperature = 273 K  
 Total area of solid surface =  $10^2 \text{ cm}^2$   
 Number of active sites per unit area =  $10^{24} \text{ m}^{-2}$   
 Find number of  $O_2$  molecules adsorbed per active site.
- A 0.03 M of an acid solution in benzene is dropped on water surface, the benzene evaporates and the acid forms a monomolecular film of solid type. What volume (in ml) of the above solution would be required to cover a  $54000 \text{ cm}^2$  surface area of water with monomolecular layer of acid. Area covered by single acid molecule is  $0.3 \text{ nm}^2$  ( $N_A = 6 \times 10^{23}$ )
- The diameter of a colloidal particle is  $5000 \text{ \AA}$ . If the density of substance formed, dispersed phase, is  $4 \text{ gm/cc}$ , find the value of surface area per unit mass of colloidal particle in ( $\text{m}^2/\text{gm}$ ).
- A container contains 1 litre, 2M solution of benzene in ether. A piece of 3 kg charcoal is dipped in the solution. Molecules of benzene get adsorbed on the surface of charcoal and form monolayer. The molarity of resulting solution decreases to 1M. If surface area available for adsorption on charcoal  $12\sqrt{3} \text{ cm}^2/\text{gm}$ . Then find distance (in  $\text{\AA}$ ) between two adjacent carbon atoms in a benzene molecule.  
 (Assume: Shape of benzene molecule perfectly hexagonal.)  
 [Use:  $N_A = 6 \times 10^{23}$ ]
- $112 \text{ cm}^3$  hydrogen gas is adsorbed uniformly at the surface of 5 gm Palladium at  $273^\circ\text{C}$  and 2 atm. If the effective surface area of each hydrogen molecule is  $0.4 \text{ nm}^2$ , then the specific surface area of Palladium is :
- The desorption of gas molecules from the adsorbent surface obeys Arrhenius equation. The average time upto which a  $N_2$  molecule may remain adsorbed at Pt-surface at 400K is  
 [Given: Pre-exponential factor,  $A = 1.25 \times 10^8 \text{ s}^{-1}$  ;  
 Activation energy of desorption =  $16 \text{ Kcal}$ ,  $e^{20} = 5 \times 10^8$ ]
- A colloid prepared by the addition of KI to  $\text{AgNO}_3$  solution is purified using dialysis. Find the minimum mass in grams of an electrolyte 'AB' (GMM = 60) required to completely coagulate 1ℓ of the aforementioned colloid

Given :

| Active ion causing flocculation | Flocculation value(mmol/l) |
|---------------------------------|----------------------------|
| $A^+$                           | 50                         |
| $B^-$                           | 100                        |





## EXERCISE # O-I

Select the correct alternative. (Only one is correct)

1. Which gas will be adsorbed on a solid to greater extent.  
(A) A gas having non polar molecule  
(B) A gas having highest critical temperature ( $T_c$ )  
(C) A gas having lowest critical temperature.  
(D) A gas having highest critical pressure.
2. The heat of physisorption lie in the range of  
(A)  $1 - 10 \text{ kJ mol}^{-1}$   
(B)  $20 \text{ to } 40 \text{ kJ mol}^{-1}$   
(C)  $40 \text{ to } 200 \text{ kJ mol}^{-1}$   
(D)  $200 \text{ to } 400 \text{ kJ mol}^{-1}$
3. Adsorption is multilayer in case of  
(A) physical adsorption  
(B) chemisorption  
(C) in both  
(D) none of the these
4. Reversible adsorption is  
(A) chemical adsorption  
(B) physical adsorption  
(C) both  
(D) none
5. An emulsion is a colloidal system of  
(A) two solids  
(B) two liquids  
(C) one gas and one solid  
(D) one gas and one liquid
6. The nature of bonding forces in chemisorption  
(A) purely physical such as Van Der Waal's forces  
(B) purely chemical  
(C) both chemical and physical simultaneously.  
(D) none of these
7. The Tyndall effect associated with colloidal particles is due to  
(A) presence of electrical charges  
(B) scattering of light  
(C) absorption of light  
(D) reflection of light
8. Which one of the following is not applicable to chemisorption?  
(A) Its heat of adsorption is high  
(B) It takes place at high temperature  
(C) It is reversible  
(D) It forms mono-molecular layers
9. In the colloidal state the particle size ranges  
(A) below  $1 \text{ nm}$   
(B) between  $1 \text{ nm}$  to  $1000 \text{ nm}$   
(C) more than  $1000 \text{ nm}$   
(D) none of the above
10. Colloids can be purified by  
(A) condensation  
(B) peptization  
(C) coagulation  
(D) dialysis
11. Milk is an example of  
(A) emulsion  
(B) suspension  
(C) foam  
(D) sol.

12. Colloidal particles in a sol. can be coagulated by  
(A) heating (B) adding an electrolyte  
(C) adding oppositely charged sol (D) any of the above methods
13. Emulsifier is an agent which  
(A) accelerates the dispersion (B) homogenizes an emulsion  
(C) stabilizes an emulsion (D) aids the flocculation of an emulsion
14. Fog is a colloidal system of  
(A) gas in liquid (B) liquid in gas (C) gas in gas (D) gas in solid
15. Given below are a few electrolytes, indicate which one among them will bring about the coagulation of a gold sol. quickest and in the least of molar concentration?  
(A) NaCl (B)  $\text{MgSO}_4$  (C)  $\text{Al}_2(\text{SO}_4)_3$  (D)  $\text{K}_4[\text{Fe}(\text{CN})_6]$
16. When a lyophobic colloidal solution is observed, we can see  
(A) light scattered by colloidal particle  
(B) size of the colloidal particle  
(C) shape of the colloidal particle  
(D) relative size of the colloidal particle
17. The electrical charge on a colloidal particle is indicated by  
(A) Brownian movement (B) electrophoresis  
(C) ultra microscope (D) molecular sieves
18. The minimum concentration of an electrolyte required to cause coagulation of a sol is called  
(A) flocculation value (B) gold number (C) protective value (D) none of these
19. Smoke precipitator works on the principle of  
(A) distribution law (B) neutralization of charge on colloids  
(C) Le-Chatelier's principle (D) addition of electrolytes
20. Which one of following statements is not correct in respect of lyophilic sols?  
(A) There is a considerable interaction between the dispersed phase and dispersion medium  
(B) These are quite stable and are not easily coagulated  
(C) They need stabilizing agent  
(D) The particles are hydrated
21.  $\text{As}_2\text{S}_3$  sol is  
(A) positive colloid (B) negative colloid (C) neutral colloid (D) none of the above
22. At the critical micelle concentration (CMC) the surfactant molecules  
(A) decompose (B) dissociate  
(C) associate (D) become completely soluble
23. Small liquid droplets dispersed in another liquid is called  
(A) suspension (B) emulsion (C) gel (D) true solution
24. The process which is catalysed by one of the product is called  
(A) acid-base catalysis (B) autocatalysis  
(C) negative catalysis (D) homogeneous catalysis

25. Tyndal effect would be observed in a  
(A) solution (B) solvent (C) precipitate (D) colloidal sol.
26. A liquid is found to scatter a beam of light but leaves no residue when passed through the filter paper. The liquid can be described as  
(A) a suspension (B) oil (C) a colloidal sol. (D) a true solution
27. The ability of an ion to bring about coagulation of a given colloid depends upon  
(A) its charge (B) the sign of the charge alone  
(C) the magnitude of the charge (D) both magnitude and sign of charge
28. An arsenious sulphide sol. carries a negative charge. The maximum precipitating power of this sol. is possessed by  
(A)  $K_2SO_4$  (B)  $CaCl_2$  (C)  $Na_3PO_4$  (D)  $AlCl_3$
29. Which of the following is an example of associated colloid?  
(A) Protein + water (B) Soap + water (C) Rubber + benzene (D)  $As_2O_3 + Fe(OH)_3$
30. Although nitrogen does not adsorb on surface at room temperature, it adsorbs on surface at 83K. Which one of the following statements is correct -  
(A) At 83K, there is formation of monomolecular layer  
(B) At 83K, there is formation of multimolecular layer  
(C) At 83K, nitrogen molecules are held by chemical bonds  
(D) At 83K, nitrogen is adsorbed as atoms.
31. Gold number of a lyophilic sol is such a property that :  
(A) The larger its value, the greater is the peptizing power  
(B) The lower its value, the greater is the peptizing power  
(C) The lower its value, the greater is the protecting power  
(D) The larger its value, the greater is the protecting power
32. Which of the following statements is incorrect regarding physisorptions ?  
(A) Under high pressure it results into multi molecular layer on adsorbent surface  
(B) Enthalpy of adsorption ( $\Delta H_{\text{adsorption}}$ ) is low and positive  
(C) It occurs because of Van der Waal's forces  
(D) More easily liquefiable gases are adsorbed readily
33. The volume of a colloidal particle  $V_c$ , volume of a solute particle in a true solution  $V_t$ , the volume of suspension particle is  $V_s$  can be arranged  
(A)  $V_c = V_t = V_s$  (B)  $V_s < V_c < V_t$   
(C)  $V_s > V_c > V_t$  (D)  $V_c > V_s > V_t$
34. Which of the following is not the property of physisorption -  
(A) Highly specific in nature (B) Reversible  
(C) Multilayer (D) Exothermic
35. Arrange the following electrolytes in the increasing order of coagulation power for the coagulation of  $As_2S_3$  sol -  
(I)  $Na_3PO_4$  (II)  $MgCl_2$  (III)  $AlCl_3$   
(A)  $I > II > III$  (B)  $I < II < III$  (C)  $I = III < II$  (D)  $III < I < II$

36. The gas, which is most readily adsorbed on the surface of activated charcoal is -  
(A)  $N_2$  (B)  $H_2$  (C)  $O_2$  (D)  $SO_2$
37. The migration of colloidal particles under the influence of an electrical field is known as  
(A) electro osmosis (B) electrophoresis  
(C) electrodialysis (D) None
38. Which reaction show the use of heterogenous catalyst  
(A)  $2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$   
(B)  $2SO_2(g) + O_2(g) \xrightarrow{Pt(s)} 2SO_3(g)$   
(C)  $CH_3COOCH_3(l) + H_2O(l) \xrightarrow{HCl(l)} CH_3COOH(aq.) + CH_3OH(aq.)$   
(D) All of the above
39. Promoters and Poison are the substance use in chemical reaction which  
(A) Enhance and decrease the activity of catalyst respectively  
(B) Decrease and enhance the activity of catalyst respectively  
(C) Do not have any effect on catalyst  
(D) Can be used in place of catalyst whenever required
40. Peptization process may be defined as  
(A) Formation of precipitate by adding two ionic solution  
(B) Conversion of colloidal sol into precipitate  
(C) Conversion of precipitate into colloidal sol  
(D) Enrichment precipitate from solution

## EXERCISE # O-II

(More than one may be correct)

1. Which of the following is/are correct statements  
(A) Hardy Schulz rule is related to coagulation  
(B) Brownian movement and Tyndall effect are shown by colloids  
(C) When liquid is dispersed in liquid, it is called gel.  
(D) Gold number is a measure of protective power of lyophilic colloid.
2. Which statements is/are correct?  
(A) Physical adsorption is multilayer non-directional and non specific  
(B) Chemical adsorption is generally monolayer and specific in nature  
(C) Physical adsorption is due to free valence of atoms  
(D) Chemical adsorption is stronger than physical adsorption
3. Which statement/s is/are correct  
(A) A solution is prepared by addition of excess of  $\text{AgNO}_3$  solution in KI solution. The charge likely to develop on colloidal particle is positive.  
(B) The effects of pressure on physical adsorption is high if temperature is low.  
(C) Gold number is the index for extent of gold plating done.  
(D) None
4. Colloidal solution can be purified by  
(A) Dialysis (B) Electrodialysis (C) Electrophoresis (D) Ultrafiltration
5. Which of the following is not lyophilic  
(A) Gelatin sol (B) Silver sol (C) Sulphur sol (D)  $\text{As}_2\text{S}_3$  sol
6. Colloidal Gold can be prepared by  
(A) Bredig's arc method (B) Reduction of  $\text{AuCl}_3$   
(C) Hydrolysis (D) Peptization
7. On adding  $\text{AgNO}_3$  solution into KI solution, colloidal sol can be obtained from.  
(A) 100 mL of 0.1 M  $\text{AgNO}_3$  + 100 of 0.1 M KI  
(B) 100 mL of 0.1 M  $\text{AgNO}_3$  + 100 of 0.2 M KI  
(C) 100 mL of 0.2 M  $\text{AgNO}_3$  + 100 of 0.1 M KI  
(D) 100 mL of 0.15 M  $\text{AgNO}_3$  + 100 of 0.25 M KI

**Question No. 8 to 10 (3 questions)**

Whenever a mixture of gases is allowed to come in contact with a particular adsorbent under the same conditions, the more strong adsorbate is adsorbed to greater extent irrespective of its amount present, e.g.  $\text{H}_2\text{O}$  is adsorbed to more extent on silica gel than  $\text{N}_2$  and  $\text{O}_2$ . This shows that some adsorbates are preferentially adsorbed. It is also observed that preferentially adsorbable adsorbate can displace a weakly adsorbed substance from the surface of an adsorbent.

8. Which of the following gases is adsorbed to maximum extent:  
(A) He (B) Ne (C) Ar (D) Xe



9. Which of the gas can displace remaining all the gases  
(A)  $O_2$  (B)  $N_2$  (C) CO (D)  $H_2$
10. When temperature is increased  
(A) extent of adsorption increases  
(B) extent of adsorption decreases  
(C) no effect on adsorption  
(D) extent of adsorption first decreases, then increases

**Question No. 11 to 12 (2 questions)**

In macromolecular type of colloids, the dispersed particles are themselves large molecules (usually polymers). Since these molecules have dimensions comparable to those of colloidal particles, their dispersions are called macromolecular colloids. Most lyophilic sols belong to this category. There are certain colloids which behave as normal strong electrolytes at low concentrations, but exhibit colloidal properties at higher concentrations due to the formation of aggregated particles. These are known as micelles or associated colloids. Surface active agents like soaps and synthetic detergents belong to this class.

CMC increases with the total surfactant concentration. At concentration higher than CMC, they form extended parallel sheets known as **lamellar micelles** which resemble biological membranes. With two molecules thick, the individual molecule is perpendicular to the sheets such that hydrophilic groups are on the outside in aqueous solution and on the inside is a non-polar medium.

In concentrated solutions, micelles take the form of long cylinders packed in hexagonal arrays and are called lyotropic mesomorphs.

In an aqueous solution (polar medium), the polar group points towards the periphery and the hydrophobic hydrocarbon chains point towards the centre forming the core of the micelle.

-They are capable of forming ions

-Molecules of soaps and detergents consist of lyophilic as well as lyophilic parts which associate together to form micelles.

-Micelles may contain as many as 100 molecules or more.

11. Select incorrect statement(s):  
(A) Surface active agent like soaps and synthetic detergents are micelles  
(B) Soaps are emulsifying agents  
(C)  $C_{17}H_{35}$  (hydrocarbon part) and  $-COO^-$  (carboxylate) part of stearate ion ( $C_{17}H_{35}COO^-$ ) both are hydrophobic  
(D) All are incorrect statements
12. Cleansing action of soap occurs because:  
(A) oil and grease can be absorbed into the hydrophobic centres of soap micelles and washed away  
(B) oil and grease can be absorbed into hydrophilic centres of soap micelles and washed away  
(C) oil and grease can be absorbed into both hydrophilic and hydrophobic centres but not washed away  
(D) cleansing action is not related to micelles

**Question No.13 to 15 (3 questions)**

The protective power of the lyophilic colloids is expressed in terms of gold number a term introduced by Zsigmondy. Gold number is the number of milligram of the protective colloid which prevent the coagulation of 10 ml of red gold sol. when 1 ml of a 10 percent solution of sodium chloride is added to it. Thus, smaller the gold number of lyophilic colloid, the greater is the protective power.

13. On addition of one mL solution of 10% NaCl to 10 mL of red gold sol in presence of 0.025 g of starch, the coagulation is just prevented. The gold number of starch is  
(A) 0.025 (B) 0.25 (C) 2.5 (D) 25
14. Which of the following statement(s) is/are correct  
(A) Higher the gold number, more protective power of colloid  
(B) Lower the gold number, more the protective power  
(C) Higher the coagulation value, more the coagulation power  
(D) Lower the coagulation value, higher the coagulation power
15. Gold number gives an indication of  
(A) protective nature of colloids  
(B) purity of gold in suspension  
(C) the charge on a colloidal solution of gold  
(D) g-mole of gold per litre

**Question No. 16 & 19 (4 questions)**

These questions consist of two statements each, printed as assertion and reason, while answering these questions you are required to choose any one of the following responses.

- (A) If both assertion and reason are true and the reason is a correct explanation of assertion.  
(B) If both assertion and reason are true but reason is not a correct explanation of assertion.  
(C) If assertion is true but the reason is false.  
(D) If assertion is false but the reason is true.

16. **Assertion :** When  $\text{AgNO}_3$  is treated with excess of potassium iodide, colloidal particles gets attracted towards anode.  
**Reason :** Precipitate adsorb common ions (excess) and thus become charged.
17. **Assertion :** For adsorption  $\Delta G$ ,  $\Delta H$ ,  $\Delta S$  all have -ve values  
**Reason :** Adsorption is a spontaneous exothermic process in which randomness decreases due to force of attraction between adsorbent and adsorbate.
18. **Assertion :** A gas with higher critical temperature gets adsorbed to more extent than a gas with lower critical temperature.  
**Reason :** The easily liquifiable gases get adsorbed to less extent.
19. **Assertion :** Micelles are formed by surfactant molecules above the critical micellar concentration (CMC).  
**Reason :** The conductivity of a solution having surfactant molecules decreases sharply at the CMC.

## LIST TYPE :

20.

## List-I

- (P) Inversion of can sugar  
(Q) Conversion of starch into maltose  
(R) Conversion of glucose into ethyle  
(S) Conversion of milk into curd

## List-II

- (1) Diastase  
(2) Lactor bacilli enzyme  
(3) Invertase  
(4) Zymase

## Code:

|     | P | Q | R | S |
|-----|---|---|---|---|
| (A) | 3 | 4 | 1 | 2 |
| (B) | 3 | 4 | 2 | 1 |
| (C) | 3 | 1 | 4 | 2 |
| (D) | 2 | 4 | 1 | 2 |

EXERCISE # J-MAIN

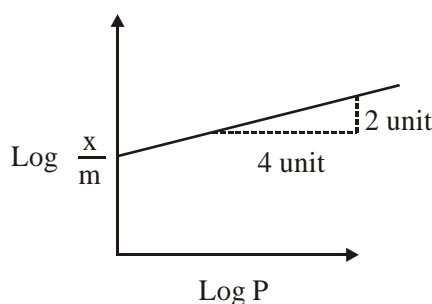
- Which of the following statements is incorrect regarding physisorptions ? [AIEEE-2009]
  - Under high pressure it results into multi molecular layer on adsorbent surface
  - Enthalpy of adsorption ( $\Delta H_{\text{adsorption}}$ ) is low and positive
  - It occurs because of Van der Waal's forces
  - More easily liquefiable gases are adsorbed readily
- According to Freundlich adsorption isotherm, which of the following is correct ? [AIEEE-2012]
  - $\frac{x}{m} \propto p^0$
  - $\frac{x}{m} \propto p^1$
  - $\frac{x}{m} \propto p^{1/n}$
  - All the above are correct for different ranges of pressure
- The coagulating power of electrolytes having ions  $\text{Na}^+$ ,  $\text{Al}^{3+}$  and  $\text{Ba}^{2+}$  for arsenic sulphide sol increases in the order :- [J-Main 2013]
 

|                                                     |                                                     |
|-----------------------------------------------------|-----------------------------------------------------|
| (1) $\text{Al}^{3+} < \text{Ba}^{2+} < \text{Na}^+$ | (2) $\text{Na}^+ < \text{Ba}^{2+} < \text{Al}^{3+}$ |
| (3) $\text{Ba}^{2+} < \text{Na}^+ < \text{Al}^{3+}$ | (4) $\text{Al}^{3+} < \text{Na}^+ < \text{Ba}^{2+}$ |
- A particular adsorption process has the following characteristics: (i) It arises due to van der Waals forces and (ii) it is reversible. Identify the correct statement that describes the above adsorption process: [J-Main 2015]
  - Enthalpy of adsorption is greater than  $100 \text{ kJ mol}^{-1}$
  - Energy of activation is low.
  - Adsorption is monolayer
  - Adsorption increases with increase in temperature.
- For a linear plot of  $\log(x/m)$  versus  $\log p$  in a Freundlich adsorption isotherm, which of the following statements is correct ? (k and n are constants) [J-Main 2016]
  - $\log (1/n)$  appears as the intercept
  - Both k and  $1/n$  appear in the slope term
  - $1/n$  appears as the intercept
  - Only  $1/n$  appears as the slope
- The Tyndall effect is observed only when following conditions are satisfied [J- Main (offline)2017]
  - The diameter of the dispersed particles is much smaller than the wavelength of the light used.
  - The diameter of the dispersed particle is not much smaller than the wavelength of the light used.
  - The refractive indices of the dispersed phase and dispersion medium are almost similar in magnitude.
  - The refractive indices of the dispersed phase and dispersion medium differ greatly in magnitude.

(1) (a) and (d)                      (2) (b) and (d)                      (3) (a) and (c)                      (4) (b) and (c)

7. Among the following, correct statement is : [J- Main (online)2017]
- (1) One would expect charcoal to adsorb chlorine more than hydrogen sulphide.
  - (2) Brownian movement is more pronounced for smaller particles than for bigger-particles.
  - (3) Hardy Schulze law states that bigger the size of the ions, the greater is its coagulating power
  - (4) Sols of metal sulphides are lyophilic
8. Adsorption of a gas on a surface follows Freundlich adsorption isotherm. Plot of  $\log \frac{x}{m}$  versus  $\log p$  gives a straight line with slope equal to 0.5, then: [J- Main (online)2017]
- ( $\frac{x}{m}$  is the mass of the gas adsorbed per gram of adsorbent)
- (1) Adsorption is proportional to the square of pressure.
  - (2) Adsorption is independent of pressure.
  - (3) Adsorption is proportional to the pressure.
  - (4) Adsorption is proportional to the square root of pressure.
9. Which one of the following is not a property of physical adsorption [J- Main (online)2018]
- (1) Unilayer adsorption occurs
  - (2) Greater the surface area, more the adsorption
  - (3) Lower the temperature, more the adsorption
  - (4) Higher the pressure, more the adsorption
10. Among the following, the false statement is : [Jee-main(online)-2019(Jan.)]
- (1) Latex is a colloidal solution of rubber particles which are positively charged
  - (2) Tyndall effect can be used to distinguish between a colloidal solution and a true solution.
  - (3) It is possible to cause artificial rain by throwing electrified sand carrying charge opposite to the one on clouds from an aeroplane.
  - (4) Lyophilic sol can be coagulated by adding an electrolyte.
11. An example of solid sol is : [Jee-main(online)-2019(Jan.)]
- (1) Butter
  - (2) Gem stones
  - (3) Paint
  - (4) Hair cream
12. Adsorption of a gas follows Freundlich adsorption isotherm. In the given plot, x is the mass of the gas adsorbed on mass m of the adsorbent at pressure p.  $\frac{x}{m}$  is proportional to

[Jee-main(online)-2019(Jan.)]



- (1)  $P^{1/4}$                       (2)  $P^2$                       (3)  $P$                       (4)  $P^{1/2}$

13. Haemoglobin and gold sol are examples of : [Jee-main(online)-2019(Jan.)]  
 (1) negatively charged sols  
 (2) positively charged sols  
 (3) negatively and positively charged sols, respectively  
 (4) positively and negatively charged sols, respectively
14. Among the colloids cheese (C), milk (M) and smoke (S), the correct combination of the dispersed phase and dispersion medium, respectively is : - [Jee-main(online)-2019(Jan.)]  
 (1) C : solid in liquid; M : solid in liquid ; S : solid in gas  
 (2) C : solid in liquid; M : liquid in liquid ; S : gas in solid  
 (3) C : liquid in solid; M : liquid in solid ; S : solid in gas  
 (4) C : liquid in solid; M : liquid in liquid ; S : solid in gas
15. Peptization is a : [Jee-main(online)-2019(April)]  
 (1) process of converting a colloidal solution into precipitate  
 (2) process of converting precipitate into colloidal solution  
 (3) process of converting soluble particles to form colloidal solution  
 (4) process of bringing colloidal molecule into solution
16. Among the following, the INCORRECT statement about colloids is : [Jee-main(online)-2019(April)]  
 (1) They can scatter light  
 (2) They are larger than small molecules and have high molar mass  
 (3) The range of diameters of colloidal particles is between 1 and 1000 nm  
 (4) The osmotic pressure of a colloidal solution is of higher order than the true solution at the same concentration
17. A gas undergoes physical adsorption on a surface and follows the given Freundlich adsorption isotherm equation  

$$\frac{x}{m} = kp^{0.5}$$
  
 Adsorption of the gas increases with : [Jee-main(online)-2019(April)]  
 (1) Decrease in p and decrease in T  
 (2) Increase in p and increase in T  
 (3) Increase in p and decrease in T  
 (4) Decrease in p and increase in T
18. The aerosol is a kind of colloid in which : [Jee-main(online)-2019(April)]  
 (1) gas is dispersed in solid  
 (2) solid is dispersed in gas  
 (3) liquid is dispersed in water  
 (4) gas is dispersed in liquid
19. 10 mL of 1mM surfactant solution forms a monolayer covering 0.24 cm<sup>2</sup> on a polar substrate. If the polar head is approximated as cube, what is its edge length? [Jee-main(online)-2019(April)]  
 (1) 2.0 pm                      (2) 2.0 nm                      (3) 1.0 pm                      (4) 0.1 nm

20. 0.27 g of a long chain fatty acid was dissolved in 100 cm<sup>3</sup> of hexane. 10 mL of this solution was added dropwise to the surface of water in a round watch glass. Hexane evaporates and a monolayer is formed. The distance from edge to centre of the watch glass is 10 cm. What is the height of the monolayer?

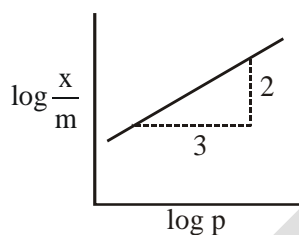
[Density of fatty acid = 0.9 g cm<sup>-3</sup>,  $\pi = 3$ ]

[Jee-main(online)-2019(April)]

- (1) 10<sup>-8</sup> m                      (2) 10<sup>-6</sup> m                      (3) 10<sup>-4</sup> m                      (4) 10<sup>-2</sup> m

21. Adsorption of a gas follows Freundlich adsorption isotherm  $x$  is the mass of the gas adsorbed on mass  $m$  of the adsorbent. The plot of  $\log \frac{x}{m}$  versus  $\log p$  is shown in the given graph.  $\frac{x}{m}$  is proportional to :

[Jee-main(online)-2019(April)]



- (1)  $p^{3/2}$                       (2)  $p^3$                       (3)  $p^{2/3}$                       (4)  $p^2$

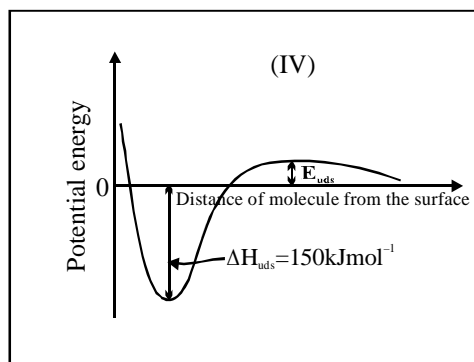
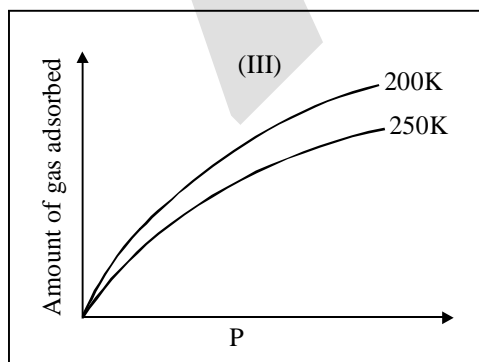
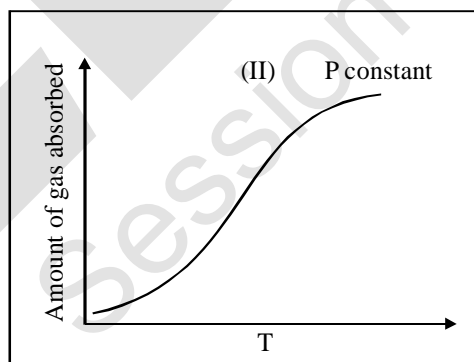
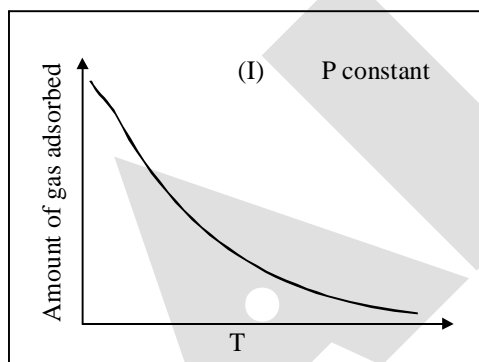
22. The correct option among the following is :

[Jee-main(online)-2019(April)]

- (1) Colloidal particles in lyophobic sols can be precipitated by electrophoresis.
- (2) Brownian motion in colloidal solution is faster the viscosity of the solution is very high.
- (3) Colloidal medicines are more effective because they have small surface area.
- (4) Addition of alum to water makes it unfit for drinking.

EXERCISE # J-ADVANCED

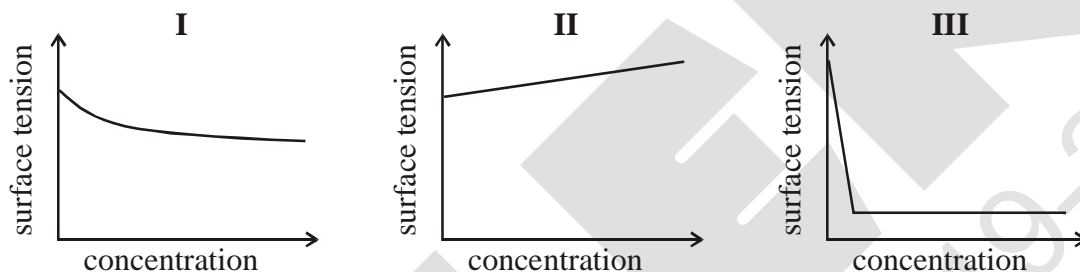
- Among the following, the surfactant that will form micelles in aqueous solution at the lowest molar concentration at ambient conditions is [JEE 2008]  
 (A)  $\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3\text{Br}^-$  (B)  $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^- \text{Na}^+$   
 (C)  $\text{CH}_3(\text{CH}_2)_6\text{COO}^- \text{Na}^+$  (D)  $\text{CH}_3(\text{CH}_2)_{11}\text{N}^+(\text{CH}_3)_3\text{Br}^-$
- Among the electrolytes  $\text{Na}_2\text{SO}_4$ ,  $\text{CaCl}_2$ ,  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{NH}_4\text{Cl}$ , the most effective coagulation agent for  $\text{Sb}_2\text{S}_3$  sol is [JEE 2009]  
 (A)  $\text{Na}_2\text{SO}_4$  (B)  $\text{CaCl}_2$  (C)  $\text{Al}_2(\text{SO}_4)_3$  (D)  $\text{NH}_4\text{Cl}$
- The correct statement(s) pertaining to the adsorption of a gas on a solid surface is (are) - [JEE 2011]  
 (A) Adsorption is always exothermic  
 (B) Physisorption may transform into chemisorption at high temperature  
 (C) Physisorption increases with increasing temperature but chemisorption decreases with increasing temperature  
 (D) Chemisorption is more exothermic than physisorption, however it is very slow due to higher energy of activation
- Choose the correct reason(s) for the stability of the **lyophobic** colloidal particle. [JEE 2012]  
 (A) Preferential adsorption of ions on their surface from the solution  
 (B) Preferential adsorption of solvent on their surface from the solution  
 (C) Attraction between different particles having opposite charges on their surface  
 (D) Potential difference between the fixed layer and the diffused layer of opposite charges around the colloidal particles
- The given graphs / data **I, II, III and IV** represent general trends observed for different physisorption and chemisorption processes under mild conditions of temperature and pressure. Which of the following choice(s) about **I, II, III and IV** is (are) correct ? [JEE 2012]



- (A) **I** is physisorption and **II** is chemisorption (B) **I** is physisorption and **III** is chemisorption  
 (C) **IV** is chemisorption and **II** is chemisorption (D) **IV** is chemisorption and **III** is chemisorption



6. Methylene blue, from its aqueous solution, is adsorbed on activated charcoal at  $25^{\circ}\text{C}$ . For this process, the correct statement is - [J. Adv. 2013]
- (A) The adsorption requires activation at  $25^{\circ}\text{C}$
- (B) The adsorption is accompanied by a decrease in enthalpy
- (C) The adsorption increases with increase of temperature
- (D) The adsorption is irreversible
7. The qualitative sketches I, II and III given below show the variation of surface tension with molar concentration of three different aqueous solutions of KCl,  $\text{CH}_3\text{OH}$  and  $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^- \text{Na}^+$  at room temperature. The correct assignment of the sketches is - [J. Adv. 2016]

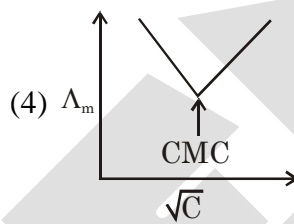
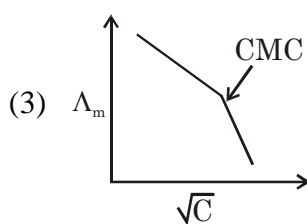
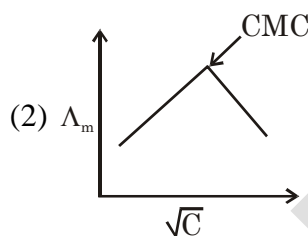
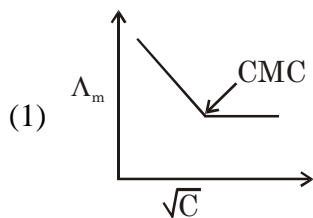


- (A) I : KCl                      II :  $\text{CH}_3\text{OH}$                       III :  $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^- \text{Na}^+$
- (B) I :  $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^- \text{Na}^+$                       II :  $\text{CH}_3\text{OH}$                       III : KCl
- (C) I : KCl                      II :  $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^- \text{Na}^+$                       III :  $\text{CH}_3\text{OH}$
- (D) I :  $\text{CH}_3\text{OH}$                       II : KCl                      III :  $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^- \text{Na}^+$
8. The correct statement(s) about surface properties is (are) [JEE 2017]
- (A) Cloud is an emulsion type of colloid in which liquid is dispersed phase and gas is dispersion medium
- (B) Adsorption is accompanied by decrease in enthalpy and decrease in entropy of the system.
- (C) Brownian motion of colloidal particles does not depend on the size of the particles but depends on viscosity of the solution.
- (D) The critical temperatures of ethane and nitrogen are 563 K and 126 K, respectively. The adsorption of ethane will be more than that of nitrogen on same amount of activated charcoal at a given temperature.

9. Molar conductivity ( $\Lambda_m$ ) of aqueous solution of sodium stearate, which behaves as a strong electrolyte, is recorded at varying concentration( $c$ ) of sodium stearate. Which one of the following plots provides the correct representation of micelle formation in the solution ?

(Critical micelle concentration (CMC) is marked with an arrow in the figures.)

[JEE 2019]



**ANSWER-KEY****EXERCISE # S-I**

- |              |              |              |
|--------------|--------------|--------------|
| 1. Ans.(200) | 2. Ans.(0.6) | 3. Ans (1)   |
| 4. Ans.(5)   | 5. Ans.(3)   | 6. Ans.(30)  |
| 7. Ans.(5)   | 8. Ans.(9)   | 9. Ans.(600) |
| 10. Ans.(4)  |              |              |

**EXERCISE # S-II**

- |                       |                                                  |                         |
|-----------------------|--------------------------------------------------|-------------------------|
| 1. Ans.(3)            | 2. Ans. (1)                                      | 3. Ans. (3)             |
| 4. Ans.(2)            | 5. Ans. $2.4 \times 10^6 \text{ cm}^2/\text{gm}$ |                         |
| 6. Ans. 4 sec         | 7. Ans. (6)                                      | 8. Ans. $\frac{3}{140}$ |
| 9. $2.35 \times 10^9$ | 10. Ans. $10^4$ times                            |                         |

**EXERCISE # O-I**

- |              |             |             |
|--------------|-------------|-------------|
| 1. Ans. (B)  | 2. Ans. (B) | 3. Ans. (A) |
| 4. Ans.(B)   | 5. Ans.(B)  | 6. Ans.(B)  |
| 7. Ans.(B)   | 8. Ans.(C)  | 9. Ans.(B)  |
| 10. Ans.(D)  | 11. Ans.(A) | 12. Ans.(D) |
| 13. Ans.(C)  | 14. Ans.(B) | 15. Ans.(C) |
| 16. Ans.(A)  | 17. Ans.(B) | 18. Ans.(A) |
| 19. Ans.(B)  | 20. Ans.(C) | 21. Ans.(B) |
| 22. Ans.(C)  | 23. Ans.(B) | 24. Ans.(B) |
| 25. Ans. (D) | 26. Ans.(C) | 27. Ans.(D) |
| 28. Ans.(D)  | 29. Ans.(B) | 30. Ans.(B) |
| 31. Ans.(C)  | 32. Ans.(B) | 33. Ans.(C) |
| 34. Ans.(A)  | 35. Ans.(B) | 36. Ans.(D) |
| 37. Ans.(B)  | 38. Ans.(B) | 39. Ans.(A) |
| 40. Ans.(C)  |             |             |

**EXERCISE # O-II**

- |                |                |               |
|----------------|----------------|---------------|
| 1. Ans.(A,B,D) | 2. Ans.(A,B,D) | 3. Ans.(A, B) |
| 4. Ans.(A,B,D) | 5. Ans.(B,C,D) | 6. Ans.(A, B) |
| 7. Ans.(B,C,D) | 8. Ans.(D)     | 9. Ans.(C)    |
| 10. Ans.(B)    | 11. Ans.(A, C) | 12. Ans.(A)   |
| 13. Ans.(D)    | 14. Ans.(B, D) | 15. Ans.(A)   |
| 16. Ans.(A)    | 17. Ans.(A)    | 18. Ans.(C)   |
| 19. Ans.(B)    | 20. Ans.(C)    |               |

**EXERCISE # J-MAIN**

- |             |             |              |
|-------------|-------------|--------------|
| 1. Ans.(2)  | 2. Ans. (4) | 3. Ans. (2)  |
| 4. Ans.(2)  | 5. Ans. (4) | 6. Ans. (2)  |
| 7. Ans. (2) | 8. Ans. (4) | 9. Ans. (1)  |
| 10. Ans.(1) | 11. Ans.(2) | 12. Ans.(4)  |
| 13. Ans.(4) | 14. Ans.(4) | 15. Ans.(2)  |
| 16. Ans.(4) | 17. Ans.(3) | 18. Ans. (2) |
| 19. Ans.(1) | 20. Ans.(2) | 21. Ans.(3)  |
| 22. Ans.(1) |             |              |

**EXERCISE # J-ADVANCED**

- |              |              |                  |
|--------------|--------------|------------------|
| 1. Ans.(A)   | 2. Ans.(C)   | 3. Ans.(A, B, D) |
| 4. Ans.(A,D) | 5. Ans.(A,C) | 6. Ans.(B)       |
| 7. Ans.(D)   | 8. Ans.(B,D) | 9. Ans.(3)       |

## RADIOACTIVITY

### 1. NUCLEAR CHEMISTRY

Nuclear chemistry deals with the phenomenon related with nucleus, like Radioactivity, Nuclear fission and fusion reactions, etc.

### 2. NUCLEAR STABILITY

The number of discovered elements till date is 118. All have some isotopes. The total number of isotopes is about 2000. Among these isotopes, the number of non-radioactive isotopes is even less than 300. Most of the isotopic forms have unstable nucleus due to very strong protonic repulsion. These unstable nuclei undergo spontaneous disintegration, causing radioactivity.

The stability of few nuclei against very strong protonic repulsion may be explained by the following theories :

#### 2.1 NUCLEAR FORCE THEORY :

Nuclear force is an imaginary force which holds the nucleons together.

- i. The exact nature of force is not known because it does not obey inverse square law.
- ii. It is a very short range force & it drops to 0 at  $10^{-14}\text{m}$ . The nuclear force becomes repulsive at very small distance ( $8 \times 10^{-16}\text{m}$ ).
- iii. Nuclear force acts equally between all the nucleons.  $p-p = n-n = n-p$
- iv. In the stable nucleus, the nuclear force is stronger than protonic repulsion.
- v. On increasing atomic number, protonic repulsion increases. As the nuclear force can't hold the particles, nucleus becomes unstable.

#### 2.2 YUKAWA'S MESON THEORY :

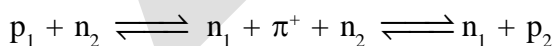
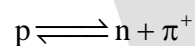
Yukawa suggested that inside the nucleus, interconversion between proton & neutron occur with the help of mesons by which nucleons hold each other.

p-meson or pions  $\pi^0 \quad \pi^+ \quad \pi^-$

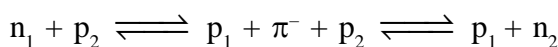
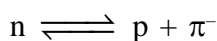
$\mu$ -meson or muons  $\mu^0 \quad \mu^+ \quad \mu^-$

mass of meson =  $(200 \text{ to } 300) \times m_e$

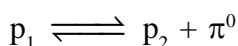
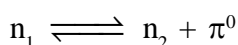
##### (i) Role of positive meson :



##### (ii) Role of negative meson :



##### (iii) Role of neutral meson :



### 2.3 MASS DEFECT AND BINDING ENERGY :

For all the isotopes (radioactive/non-radioactive), the theoretical mass (sum of masses of protons, neutrons and electrons) is greater than its isotopic (actual) mass. This difference in mass is called **mass defect** ( $\Delta m$ ). For example,

For  ${}^4_2\text{He}$ , isotopic mass = 4.0026 u

Now, Mass due to  $e^- = 2 \times 0.00054 = 0.00108\text{u}$

Mass due to p =  $2 \times 1.00727 = 2.01454\text{u}$

Mass due to n =  $2 \times 1.00867 = 2.01734\text{u}$

|       |          |
|-------|----------|
| Total | 4.03296u |
|-------|----------|

The decrease in mass is due to its conversion into energy at the time of atom formation, by Einstein equation :

$$E = \Delta m \cdot c^2$$

As this energy is released in binding the particles together, it is called

**binding energy.**

If  $\Delta m = 1 \text{ a.m.u.}$ ,

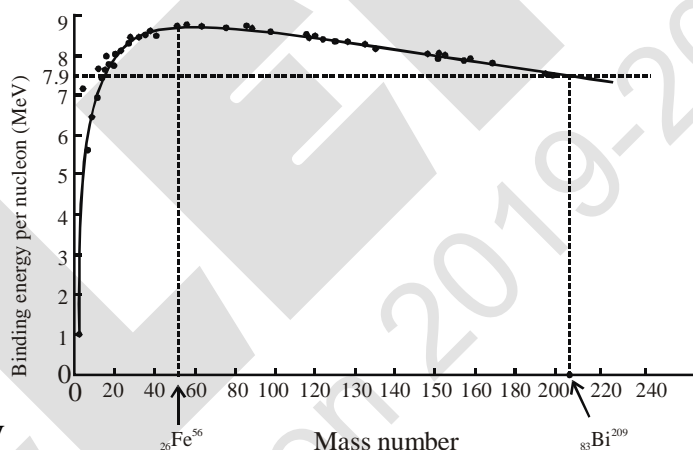
then B.E.,  $E \simeq 1.5 \times 10^{-10} \text{ J} \simeq 931.5 \text{ MeV}$

\* Binding energy per nucleon gives a quantitative measure

of nuclear stability.  $\text{B.E. per nucleon} = \frac{\text{B.E.}}{\text{No. of nucleons}}$

Greater the value of B.E. per nucleon, more is the stability of nucleus.

- (i) Nuclear binding energy is maximum for mass number 50 – 60.
- (ii) Fe, Co, Ni have very high binding energy per nucleon.
- (iii) A very heavy nucleus, say  $A = 240$ , has lower binding energy per nucleon compared to that of a nucleus with  $A = 120$ . Thus if a nucleus  $A = 240$  breaks into two  $A = 120$  nuclei, energy would be released in the process. This implies nucleons get more tightly bound. It has very important applications for energy production through fission.
- (iv) Consider two very light nuclei ( $A \leq 10$ ) joining to form a heavier nucleus. The binding energy per nucleon of the heavier nuclei is more than the binding energy per nucleon of the lighter nuclei, again energy would be released in such a process of fusion.
- (v) All the nuclei having BE/nucleon greater than 7.9 MeV are stable. The value 7.9 is not applicable for lighter nuclei because they may be stable even at lower value.



**Ex.1.** Calculate BE/nucleon for  ${}_{17}\text{Cl}^{35}$

$$m_e = 0.00054 \text{ u}, m_p = 1.00727 \text{ u}, m_n = 1.00867 \text{ u}$$

**Sol.**  $\Delta m = (17 \times 0.00054 + 17 \times 1.00727 + 18 \times 1.00867) - 35 = 0.28883 \text{ u}$

$$\text{B.E.} = 0.28883 \times 931.5 = 269.045 \text{ MeV}$$

$$\therefore \text{B.E. nucleon} = \frac{269.045}{35} = 7.687 \text{ MeV}$$

**Ex.2.** Calculate BE for an additional neutron in  ${}_3\text{Li}^6$  nucleus. Nuclear mass of  $\text{Li}^6 = 6.0025$ ,  $\text{Li}^7 = 7.0081$ ,  $m_n = 1.0087 \text{ u}$

**Sol.**  ${}_3\text{Li}^6 + {}_0\text{H}^1 \rightarrow {}_3\text{Li}^7$

$$\Delta m = (6.0025 + 1.0087) - 7.0081 = 0.0031 \text{ u}$$

$$\therefore \text{Energy released} = 0.0031 \times 931.5 = 2.888 \text{ MeV}$$

**Ex.3.** A nucleus  $A^{240}$  (BE/nucleon = 7.3 MeV) dissociate into two identical nuclei  $B^{120}$ , (BE/nucleon = 8.2 MeV). Calculate the amount of energy absorbed or released.

**Sol.** Energy released =  $2 \times 120 \times 8.2 - 240 \times 7.3 = 216 \text{ MeV}$

## 2.4 PACKING FRACTION :

'Aston' expressed relation between isotopic mass & mass number in terms of packing fraction.

### ◆ Packing Fraction

$$= \frac{\text{Atomic mass} - \text{Mass number}}{\text{Mass number}} \times 10^4$$

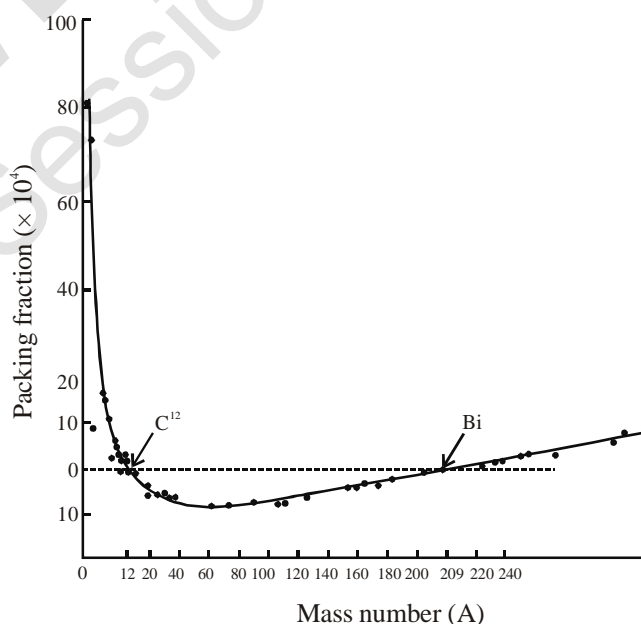
\* packing fraction of C-12 is exactly zero.

\* packing fraction may be positive or negative

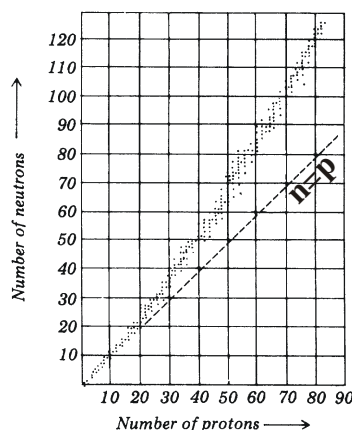
\* negative packing fraction implies that nuclei is stable

\* positive packing fraction implies that nuclei is unstable

\* Some lighter nuclei have positive packing fraction although nucleus is stable



## 2.5. NEUTRON / PROTON RATIO AND STABILITY BELT :



- ◆ All the stable nuclei lie in a zone or belt of stability, as shown in the figure.
- ◆ None of the stable nucleus have  $\frac{n}{p}$  ratio less than 1 (except  ${}^1_1\text{H}^1$ ) and greater than 1.52 ( $\frac{n}{p}$  ratio of heaviest stable nucleus  ${}_{83}\text{Bi}^{209}$ ).
- ◆ In lighter nuclei ( $Z < 20$ ),  $\frac{n}{p}$  ratio of stable nuclei is very close to 1.

## 2.6 EVEN ODD THEORY :

The number of stable nuclides is maximum when both protons and neutrons are even numbers.

| p    | n    | No. of stable nucleus | Examples                                                                                                   |
|------|------|-----------------------|------------------------------------------------------------------------------------------------------------|
| even | even | ~ 165                 | ${}^4_2\text{He}$ , ${}^{12}_6\text{C}$ , ${}^{16}_8\text{O}$ , etc                                        |
| even | odd  | ~ 55                  | ${}^9_4\text{Be}$ , ${}^{13}_6\text{C}$ , ${}^{17}_8\text{O}$ , etc                                        |
| odd  | even | ~ 50                  | ${}^7_3\text{Li}$ , ${}^{11}_5\text{B}$ , ${}^{19}_9\text{F}$ , etc                                        |
| odd  | odd  | 5                     | ${}^2_1\text{H}$ , ${}^6_3\text{Li}$ , ${}^{10}_5\text{B}$ , ${}^{14}_7\text{N}$ , ${}^{180}_{73}\text{T}$ |

- ◆ Nearly 60% of stable nuclei have even number of protons and neutrons.

## 2.7 MAGIC NUMBERS :

Nuclei with 2, 8, 20, 50, 82 or 126 protons or neutrons are exceptionally stable and have a larger number of stable isotopes than neighboring nuclei in the periodic table. These numbers are called magic numbers. They are supposed to represent completely filled nuclear shells or energy levels.

e.g.  ${}_{50}\text{Sn}$  having 10 stable isotopes while  ${}_{51}\text{Sb}$  has only two stable isotopes.

- ◆ Nuclei with magic number of protons as well as neutrons have notably high stabilities. [eg.  ${}^4_2\text{He}$ ,  ${}^{16}_8\text{O}$ ,  ${}^{40}_{20}\text{Ca}$  and  ${}^{208}_{82}\text{Pb}$ ].



### 3. RADIO ACTIVITY

The spontaneous emission of particles, electromagnetic radiation or both by unstable nuclei, is known as radioactivity. Only unstable nuclei exhibit this property.

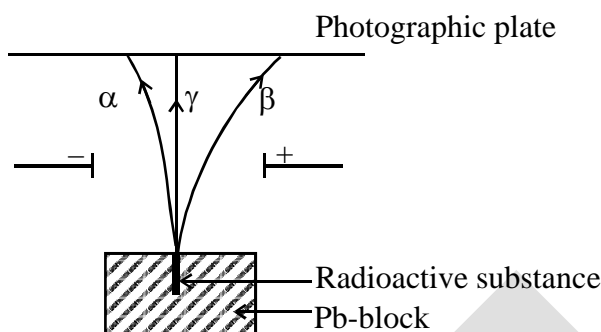
This phenomenon (radioactivity) was discovered by Henry Becquerel. On working with uranium salt, he observed that some radiations having the following properties come out from these salts:

- (i) They blacken the photographic plates.
- (ii) They cause fluorescence on ZnS screen.
- (iii) They ionise the gas through which they pass.

He gave the name **becquerel rays** to these radiations.

Later on, **Madam Curie** discovered two elements Radium (Ra) and Polonium (Po). She found that these elements as well as their salts emit similar radiations. She generalised the name of Becquerel rays as **radioactive rays** and the phenomenon, as **radioactivity**.

### 4. NATURE OF RADIOACTIVE RAYS



#### 4.1 PROPERTIES OF $\alpha$ , $\beta$ -PARTICLES AND $\gamma$ -RAYS :

|     | Properties                     | Alpha                         | Beta                                                 | Gamma                                          |
|-----|--------------------------------|-------------------------------|------------------------------------------------------|------------------------------------------------|
| 1.  | Nature                         | Fast moving He nuclei         | Fast moving electrons                                | Electromagnetic radiation of very high energy. |
| 2.  | Representation                 | ${}_2\text{He}^4$ or $\alpha$ | ${}_{-1}\text{e}^0$ or ${}_{-1}\beta^0$ or $\beta^-$ | $\gamma$ or ${}_0^0\gamma$                     |
| 3.  | Charge                         | 2 unit (+ve)                  | 1 unit (-ve)                                         | no charge                                      |
| 4.  | Velocity                       | 10-20% of speed of light      | 33% to 90% of speed of light                         | Same as light waves                            |
| 5.  | Relative penetrating power     | 1<br>(0.01 mm of Al foil)     | 100<br>(0.1 cm Al foil)                              | 10000<br>(8 cm lead or 25 cm steel)            |
| 6.  | Travel distance in air (Range) | 2 – 4 cm                      | 200 – 300 cm                                         | –                                              |
| 7.  | Kinetic energy                 | high                          | low                                                  | –                                              |
| 8.  | Effect on ZnS plate            | Luminosity                    | Little effect                                        | –                                              |
| 9.  | Mass g/particle                | $6.64 \times 10^{-27}$ kg     | $9.109 \times 10^{-31}$ kg                           | –                                              |
| 10. | Relative ionising power        | 10000                         | 100                                                  | 1                                              |

4.2.  $\alpha$ -DECAY :

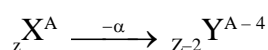
If any  $\alpha$ -emitter is taken in a closed vessel, after sufficient time, presence of He gas is observed in the vessel. It is experimental fact considering  $\alpha$ -particle as  $\text{He}^{2+}$  ion or He nucleus.

It is assumed that inside the nuclei, some p & n exists as a  $\alpha$ -particle due to the following facts :

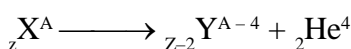
- Initially all the lighter nuclides ( $Z \leq 19$ ) were transmuted by  $\alpha$ -particles except  ${}^4_2\text{He}$ ,  ${}^8_4\text{Be}$ ,  ${}^{12}_6\text{C}$ . These nuclides were supposed to have 1, 2 and 3  $\alpha$ -particles respectively.
- Among the lighter nucleides, BE/nucleon for He is exceptionally high ( $\approx 7\text{MeV}$ ). Hence the combination of 2p & 2n as  $\alpha$ -particles is considered stable combination.
- Among p, n, deuteron (d) &  $\alpha$ -decay, Q value is positive only for  $\alpha$ -decay (energy is released). Hence among these decay,  $\alpha$ -decay is only spontaneous decay.

(i) Effects of  $\alpha$ -decay :

- The atomic number decreases by two units and mass number by 4 units per decay.



- n/p ratio increases on  $\alpha$ -decay.
- Isodiaphers are formed. Isodiaphers are the atoms of different elements having the same number of excess neutron over proton. [Same  $[N - P]$  difference.]

(ii) Q-value for  $\alpha$ -emission :

$$\Delta m = (\text{nucleidic mass } {}_Z\text{X}^A) - (\text{nucleidic mass } {}_{Z-2}\text{Y}^{A-4} + {}^4_2\text{He})$$

$$= \text{Atomic mass of } {}_Z\text{X}^A - \text{At mass of } ({}_{Z-2}\text{Y}^{A-4} + {}^4_2\text{He})$$

$$\text{Now, } Q = \Delta m c^2 = \Delta m \times 931.5 \text{ MeV.}$$

(iii) KE of emitted  $\alpha$ -particle :

$$Q \text{ value} = (\text{KE})_{\alpha} + (\text{KE})_{\text{Y}}$$

$$\& \quad (mV)_{\alpha} = (mV)_{\text{Y}}$$

$$(\text{KE})_{\alpha} = \frac{m_{\text{Y}}}{m_{\text{Y}} + m_{\alpha}} \times Q = \frac{A-4}{A} Q$$

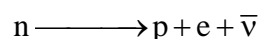


All the  $\alpha$ -particle emitted out from a particular radio-nuclide must have same KE, if the contribution of  $\gamma$ -photon is neglected.

4.3  $\beta$ -DECAY :

On  $\beta$ -decay, the atomic species get changed and hence  $\beta$  decay is always due to some nuclear change.

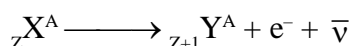
- A neutron breaks into proton, electron & anti-neutrino. As e and anti-neutrino can never exist in the nucleus, they come out.



(ii) Effect of  $\beta$ -decay :

- The atomic number increases by one unit but the mass number remains unchanged.
- n/p ratio decreases.
- Isobars are formed. (Atom of different elements having same mass number)
- Isotopes are formed by the sequential decay of  $1\alpha$  &  $2\beta$  particles. (Atoms of same element having different mass numbers.)
- Normally a radio nuclide either undergoes  $\alpha$  or  $\beta$  decay. There are very few radio nucleides which undergo simultaneous  $\alpha$  &  $\beta$  decay.

(iii) Q-value



$$\Delta m = \text{nucleidic mass } [{}_Z^AX^A - ({}_{Z+1}Y^A + m_e + m_{\bar{\nu}})]$$

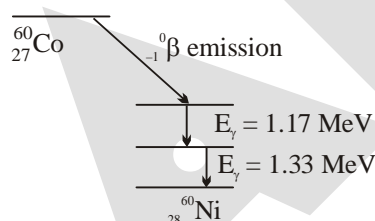
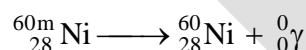
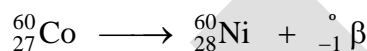
$$= \text{At mass } ({}_Z^AX^A - {}_{Z+1}Y^A)$$

$$Q = \Delta mc^2$$

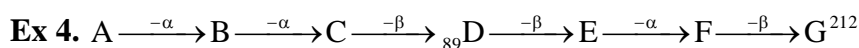
- (iv) **K.E. of  $\beta$ -particle :** The Q value will be shared between emitted  $\beta$ -particles & antineutrino. Hence KE of  $\beta$ -particles may have any value from 0 to Q value. The  $\beta$ -particle emitted out from a particular radionuclide may have different KE.

4.4.  $\gamma$ -DECAY :

This is a secondary phenomenon. When an  $\alpha$  or  $\beta$  decay takes place, the daughter nucleus generally formed is in excited state & comes to ground state by a single or successive transitions by emitting electromagnetic radiations i.e.  $\gamma$  rays.



- The atomic number & mass number remain unchanged.
- Nuclear isomers are formed. They have same nuclear composition but different energy.



- (i) Identify isotopic pairs

**Sol.** (B, E) ; (C, F) ; (D, G)

- (ii) What is the atomic & mass number of A

**Sol.** 92, 224

Ex 5. Which of the following may be the disintegration product of  ${}_{92}\text{U}^{238}$

- I. (a)  ${}_{90}\text{Th}^{234}$  (b)  ${}_{88}\text{Ra}^{232}$  (c)  ${}_{85}\text{Ra}^{235}$  (d)  ${}_{87}\text{Fr}^{227}$   
 (a)  
 II. (a)  ${}_{88}\text{Ra}^{230}$  (b)  ${}_{89}\text{Ac}^{230}$  (c)  ${}_{87}\text{Fr}^{230}$  (d)  ${}_{87}\text{Fr}^{226}$   
 (e)  ${}_{86}\text{Rn}^{226}$

Sol. (a, b, d, e)

Ex 6. Russian and American scientist have artificially prepared elements with atomic number greater than

100. The number of alpha and beta particles produced when one atom of  ${}_{103}^{257}\text{Lr}$  decay after being produced by artificial means to its stable product is -

- (A) 4  $\alpha$  and 5  $\beta$  (B) 4  $\alpha$  and 12  $\beta$  (C) 12  $\alpha$  and 4  $\beta$  (D) 12  $\alpha$  and 5  $\beta$

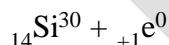
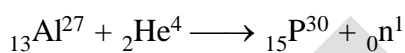
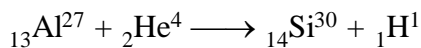
Sol. 6. Ans. (C)



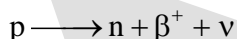
#### 4.5 POSITRON DECAY :

Given by Irene Curie and F. Juliot.

When  $\text{Mg}^{24}$ ,  $\text{Al}^{27}$  or  $\text{B}^{10}$  were bombarded by  $\alpha$ -particle, emission of p, n &  $\beta^+$  (positron) occur. On stopping the bombardment, p & n emission stop but  $\beta^+$  emission continues obeying 1<sup>st</sup> order kinetics. The isotope responsible for such  $\beta^+$  emission is called artificial **radio isotope** and the phenomenon as artificial radioactivity.



In positron decay, a proton (inside the nucleus) breaks into neutron, positron and neutrino.

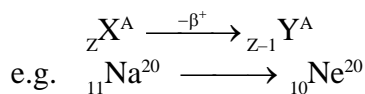


As  $\beta^+$  and  $\nu$  can never exist in the nucleus, they come out, resulting positron decay.

**Note:** A free neutron may break into proton (mass decreases) but a free proton can never break into neutron (mass increases). Inside the nucleus, both conversions are possible because of involvement of nucleus.

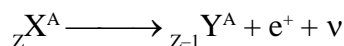
(i) **Effect of  $\beta^+$ -decay :**

- (a) The atomic number decreases by one unit but the mass number remain unchanged.



- (b) Isobars are formed.  
 (c) n/p ratio increase.

(ii) **Q-value :**



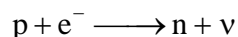
$$\Delta m = (\text{nucleidic mass of } {}_Z X^A) - (\text{nucleidic mass of } {}_{Z-1} Y^A + \text{mass of } \beta^+ + \text{mass of } \nu)$$

$$= \text{At mass } ({}_Z X^A - {}_{Z-1} Y^A) - 2m_e$$

(iii) **K.E. of  $\beta^+$  :** The KE of emitted  $e^+$  may have any value from 0 to Q-value.

#### 4.6. K-CAPTURE OR ELECTRON CAPTURE :

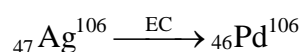
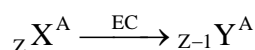
In electron capture, nucleus captures an electron of K-shell. Proton converts into neutron inside the nucleus.



As neutrino can not exist in the nucleus, it comes out.

(i) **Effects of electron capture :**

(a) Atomic number decreases by one unit but mass number remains unchanged.

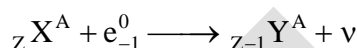


(b)  $\frac{n}{p}$  ratio increases

(c) Isobar is formed.

(d) As one electron from K-shell is captured by nucleus, electron from higher shell de-excite to K-shell, emitting X-rays.

(ii) **Q-value :**



$$\Delta m = (\text{nuclear mass of } {}_Z X^A + \text{mass of electron}) - (\text{nuclear mass of } {}_{Z-1} Y^A + \text{mass of neutrino})$$

$$= \text{Atomic mass of } {}_Z X^A - \text{Atomic mass of } {}_{Z-1} Y^A$$

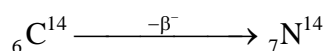
$$\text{and Q-value} = \Delta m \cdot C^2$$

(iii) **K.E. of emitted neutrino** = Q-value

#### 5. PREDICTION OF KIND OF RADIOACTIVE DECAY:

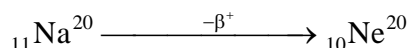
(i)  $\frac{n}{p}$  ratio increases in  $\alpha$ -decay,  $\beta^+$ -decay and electron capture but  $\frac{n}{p}$  ratio decreases in  $\beta^-$ -decay.

If the  $\frac{n}{p}$  ratio of any radioisotope is greater than that of non-radioactive (stable) isotope of the same element, the possible mode of decay is  $\beta^-$ -decay. For example,  ${}_6 C^{12}$  is non-radioactive and  ${}_6 C^{14}$  is  $\beta^-$  emitter.



$$\frac{n}{p} = \frac{8}{6} > \frac{6}{6} \text{ of } {}_6 C^{12} \quad \frac{n}{p} = \frac{7}{7}$$

If the  $\frac{n}{p}$  ratio is smaller, the possible mode of decay may be  $\alpha$ -decay or  $\beta^+$ -decay or electron capture. For example,  ${}_{11}\text{Na}^{23}$  is non-radioactive and  ${}_{11}\text{Na}^{20}$  is  $\beta^+$ -emitter.



$$\frac{n}{p} = \frac{9}{11} < \frac{12}{11} \text{ of } {}_{11}\text{Na}^{23} \quad \frac{n}{p} = \frac{10}{10}$$

- (ii) Normally,  $\alpha$ -decay occurs only in heavier nucleus
- (iii) If (atomic mass of  ${}_Z\text{X}^A$  - Atomic mass of  ${}_{Z-1}\text{Y}^A$ ) is less than mass of two electrons,  $\beta^+$ -decay is not possible (Q-value will become negative)

**Ex.7.** Predict the possible mode of radioactive decay by (i)  ${}_1\text{H}^3$  (ii)  ${}_8\text{O}^{18}$  (iii)  ${}_2\text{He}^3$  (iv)  ${}_2\text{He}^6$

**Sol.** (i)  $\left(\frac{n}{p}\right) \text{ of } {}_1\text{H}^3 = \frac{2}{1} > \left(\frac{n}{p}\right) \text{ of } {}_1\text{H}^1 \text{ or } {}_1\text{H}^2$

hence,  ${}_1\text{H}^3$  is  $\beta^-$ -emitter.

(ii)  $\left(\frac{n}{p}\right) \text{ of } {}_8\text{O}^{18} = \frac{10}{8} > \left(\frac{n}{p}\right) \text{ of } {}_8\text{O}^{16}$

hence,  ${}_8\text{O}^{18}$  is  $\beta^-$ -emitter

(iii)  $\left(\frac{n}{p}\right) \text{ of } {}_2\text{He}^3 < \left(\frac{n}{p}\right) \text{ of } {}_2\text{He}^4$

hence,  ${}_2\text{He}^3$  may be  $\beta^+$ -emitter

(iv)  $\left(\frac{n}{p}\right) \text{ of } {}_2\text{He}^6 > \left(\frac{n}{p}\right) \text{ of } {}_2\text{He}^4$

hence,  ${}_2\text{He}^6$  is  $\beta^-$ -emitter

**Ex.8.** The isotope  ${}_{71}\text{Lu}^{173}$  is neutron deficient for stability. The isotopic masses of  ${}_{71}\text{Lu}^{173}$  and stable isotope  ${}_{70}\text{Yb}^{173}$  are 172.9390 and 172.9383 amu, respectively. Predict whether  ${}_{71}\text{Lu}^{173}$  decays by  $\beta^+$ -emission or electron capture or both.

**Sol.**  $\Delta m = 172.9390 - 172.9383 = 0.0007 \text{ amu} < 2 \times \text{mass of electron}$

Hence,  ${}_{71}\text{Lu}^{173}$  can not undergo  $\beta^+$ -decay. The decay mode must be electron capture.

## 6. RADIOACTIVE DISINTEGRATION SERIES

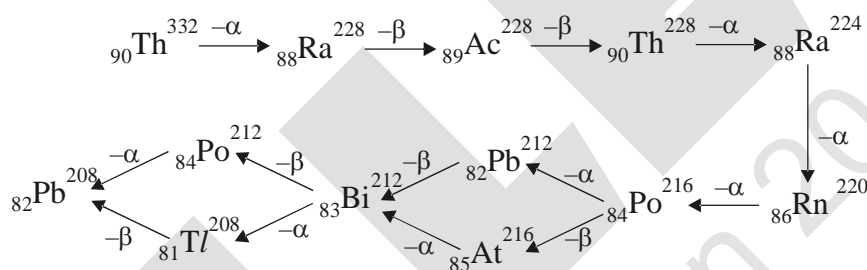
Many radioactive nucleus ( $Z > 82$ ) are obtained as a member of decay series.

The series of nuclei is known as radioactive disintegration series.

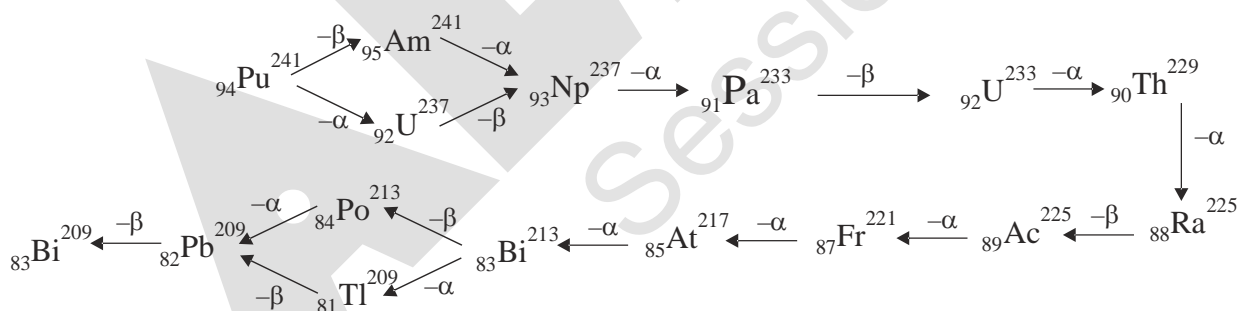
| Series                        | Parent Nucleus           | Last Nucleus             | No. of $\alpha$ -particles | No. of $\beta$ -particles |
|-------------------------------|--------------------------|--------------------------|----------------------------|---------------------------|
| 4n or<br>Thorium series       | ${}_{90}\text{Th}^{232}$ | ${}_{82}\text{Pb}^{208}$ | 6                          | 4                         |
| (4n+1) or<br>Neptunium series | ${}_{94}\text{Pu}^{241}$ | ${}_{83}\text{Bi}^{209}$ | 8                          | 5                         |
| 4n+2<br>or Uranium series     | ${}_{92}\text{U}^{238}$  | ${}_{82}\text{Pb}^{206}$ | 8                          | 6                         |
| 4n + 3<br>or Actinium series  | ${}_{92}\text{U}^{235}$  | ${}_{82}\text{Pb}^{207}$ | 7                          | 4                         |

4n, 4n + 2 and 4n + 3 series are natural while (4n + 1) is artificial.

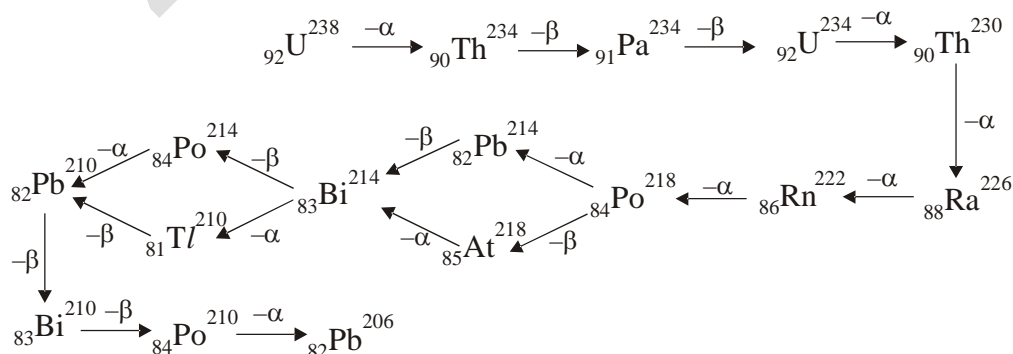
### (A) The thorium series :



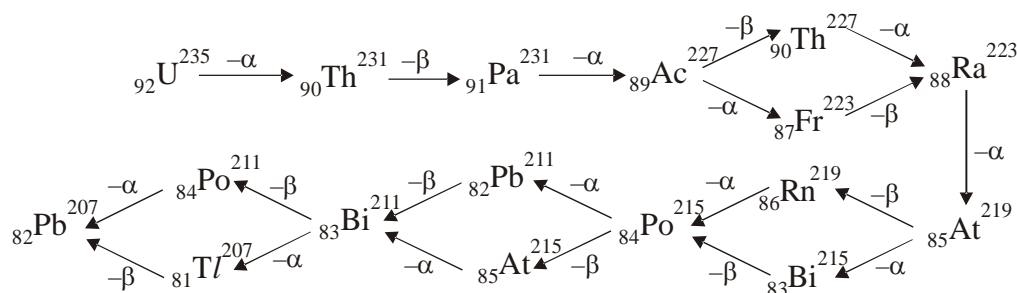
### (B) The neptunium series :



### (C) The uranium series :



## (D) The actinium series :



## 7. RATE LAW

## • Rutherford and Soddy's law :

At an instant, rate of decay or disintegration of active nuclei is directly proportional to the number of active nuclei at that instant.

$-\frac{dN}{dt}$  = rate of decay or activity (A) at time t and N = active nuclei at time t

$$-\frac{dN}{dt} \propto N \quad \text{or} \quad -\frac{dN}{dt} = \lambda N \quad \dots(i)$$

Here  $\lambda$  is the decay constant or disintegration constant, which is characteristic of that radioisotope, independent from any chemical or physical condition.

**Integral rate law :**  $N = N_0 e^{-\lambda t}$

## 7.1 UNITS OF RATE OF DECAY OR ACTIVITY :

1 Becquerel (1 Bq) = 1 dps (SI unit)

1 Curie (Ci) =  $3.70 \times 10^{10}$  dps

1 Rutherford (1 Rd) =  $10^6$  dps

• **Specific activity :** Activity of 1 gm sample of radioactive substance. Its unit is (dps per gram)

Specific activity of radium (226) is 1 Ci/gm.

• **Geiger – Muller counter** is used for detecting and counting the  $\alpha$  and  $\beta$ -particles.7.2 HALF LIFE ( $T_{1/2}$ ) :

It is the time in which half of the active nuclei decay

$$T_{1/2} = \frac{\ln 2}{\lambda} = \frac{0.693}{\lambda}$$

After 'n' half lives, the activity as well as the number of active nuclei reduced to  $\frac{1}{2^n}$  times of initial value.

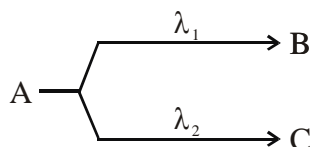


### 7.3 MEAN OR AVERAGE LIFE ( $T_{av}$ ) :

It is the average age of all active nuclei i.e.

$$T_{av} = \frac{\text{sum of times of existence of all nuclei in a sample}}{\text{initial number of active nuclei in that sample}} = \frac{1}{\lambda}$$

### 7.4 PARALLEL DECAY:



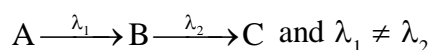
(a) The overall decay constant of A,  $\lambda = \lambda_1 + \lambda_2$

(b)  $\frac{N_B}{N_C} = \frac{\lambda_1}{\lambda_2}$

(c)  $\lambda_1 = \text{fractional yield of B} \times \lambda$

(d)  $\lambda_2 = \text{fractional yield of C} \times \lambda$

### 7.5 SEQUENTIAL DECAY :



(a) At any time, t:

$$N_A = N_A^0 \cdot e^{-\lambda_1 t}$$

$$N_B = \frac{\lambda_1 \cdot N_A^0}{\lambda_2 - \lambda_1} \cdot (e^{-\lambda_1 t} - e^{-\lambda_2 t})$$

$$N_C = N_A^0 - (N_A + N_B)$$

(b) Time for maximum nuclei of B,

$$T_{\max} = \frac{1}{\lambda_2 - \lambda_1} \cdot \ln \frac{\lambda_2}{\lambda_1}$$

(c) Maximum nuclei of B,

$$N_{B\max} = N_A^0 \cdot \left( \frac{\lambda_2}{\lambda_1} \right)^{\frac{-\lambda_2}{\lambda_2 - \lambda_1}}$$

(d) For steady state of B (radioactive equilibrium)  $\lambda_1 \cdot N_A = \lambda_2 \cdot N_B$

**Ex.9** A free neutron is unstable against  $\beta$ -decay with a half life of about 600 seconds.–

(i) Write the expression of this decay process.

(ii) If there are 600 free neutrons initially, calculate the time by which 450 of them have decayed. Also determine the initial decay rate of the sample.

**Sol.** (i)  $n \rightarrow p + e^- + \bar{\nu}$

(ii) The number of undecayed neutron would be 150 by using  $N = N_0 e^{-\lambda t}$

$$150 = 600e^{-\lambda t} \Rightarrow t = 2T_{1/2} = 1200 \text{ sec}$$

$$\text{Decay rate (initial) } R = \lambda N_0 = \frac{0.693}{600} \times 600 = 0.693 \text{ dps}$$

**Ex.10.** Obtain the amount of polonium necessary to provide a radioactivity source of 5.0 mili curie strength. The half life of polonium is 138 days.

Given : 1 curie =  $3.7 \times 10^{10}$  disintegration/sec., Avogadro number =  $6.02 \times 10^{26}$  per k-mole

**Sol.** Given :  $r = 5 \times 10^{-3} \times 3.7 \times 10^{10}$  disint./sec. &  $t_{1/2} = 138 \times 24 \times 3600$  sec and  $r = \lambda N$

$$= \frac{0.693}{t_{1/2}} N$$

$$\Rightarrow N = \frac{138 \times 24 \times 3600 \times 5 \times 3.7 \times 10^7}{0.693} = 3.18 \times 10^{15} \text{ atoms}$$

$$\therefore \text{Amount of } {}_{84}\text{Po}^{210} \text{ in grams required} = \frac{210 \times 3.18 \times 10^{15}}{6.02 \times 10^{23}} = 1.11 \times 10^{-6}$$

**Ex.11.** Calculate the radioactive disintegration constant if  $3.7 \times 10^{10}$  alpha particles are emitted by 1 gram of radium per second. Avogadro's number is  $6.03 \times 10^{23}$  and the mass number of radium is 226.

**Sol.** Activity =  $N\lambda = \left( \frac{N_A}{M_w} \times m \right) \lambda$

$$\Rightarrow 3.7 \times 10^{10} = \left( \frac{6.03 \times 10^{23}}{226} \times 1 \right) \lambda$$

$$\lambda = \frac{3.7 \times 10^{10} \times 226}{6.03 \times 10^{23}} = 1.38 \times 10^{-11} \text{ per second}$$

**Ex.12.** The half lives of X and Y are 3 minutes and 27 minutes respectively. At some instant activity of both are same, then the ratio of active nuclei of X and Y at that instant is ?

**Sol.**  $A_1 = \lambda_1 N_1$  and  $A_2 = \lambda_2 N_2$

$$A_1 = A_2 \Rightarrow \frac{0.693}{T_1} N_1 = \frac{0.693}{T_2} N_2$$

$$\Rightarrow \frac{N_1}{T_1} = \frac{N_2}{T_2} \Rightarrow \frac{N_1}{N_2} = \frac{3}{27} = \frac{1}{9}$$

$$\Rightarrow N_1 : N_2 = 1 : 9$$

**Ex.13.** Decay constant of two radioactive samples is  $\lambda$  and  $3\lambda$  respectively. At  $t = 0$ , they have equal number of active nuclei. Calculate when will be the ratio of active nuclei becomes  $e : 1$ .

**Sol.** Number of active nuclei of two radioactive sample is

$$N_1 = N_{01}e^{-\lambda t} \text{ and } N_2 = N_{02}e^{-3\lambda t}$$

$$\therefore \frac{N_1}{N_2} = \frac{e}{1} = \frac{N_{01}e^{-\lambda t}}{N_{02}e^{-3\lambda t}} = e^{2\lambda t} \quad [\because N_{01} = N_{02}]$$

$$\therefore 1 = 2\lambda t \Rightarrow t = \frac{1}{2\lambda}$$

**Ex.14.** The fraction of a radioactive sample which remains active after time  $t$  is  $\frac{9}{16}$ . What fraction remains active after  $\frac{t}{2}$  time ?

**Sol.** Active fraction  $= \frac{N}{N_0} = e^{-\lambda t}$  At time  $t$ ,  $\frac{9}{16} = e^{-\lambda t}$

$$\text{At time } t/2 \text{ active fraction} = x = e^{-\lambda t/2} = \left(e^{-\lambda t}\right)^{\frac{1}{2}}$$

$$\text{So } x = \left(\frac{9}{16}\right)^{\frac{1}{2}} = \frac{3}{4}$$

**Ex.15.** Two radioactive nuclides A and B have half life 150 min and 15 mins respectively. A fresh sample contains nuclides of B to be 32 times that of A. How much time should elapse so that number of nuclides of A becomes twice that of B ?

**Sol.** (100 sec)

$N_0$  = initial nuclides of A

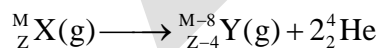
$$\text{After } t \text{ mins, } N_0 e^{-\left(\frac{\ln 2}{150}\right)t} = 2 \left[ 32 N_0 e^{-\left(\frac{\ln 2}{15}\right)t} \right] \Rightarrow t = 100 \text{ sec.}$$

**Ex.16.**  ${}^M_Z X(g) \longrightarrow {}^{M-8}_{Z-4} Y(g) + \alpha - \text{particles}$

The radioactive disintegration follows first order kinetics starting with one mole of X in a 12-litre closed flask at  $27^\circ\text{C}$ . Find the total pressure (in atm) after two half lives.

$$[R = 0.08 \text{ L atm mol}^{-1} \text{ K}^{-1}]$$

**Ans. 5**



$$t = 0 \quad 1 \text{ mol} \quad 0 \quad 0$$

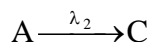
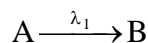
$$t = 2t_{1/2} \quad 0.25 \text{ mol} \quad 0.75 \text{ mol} \quad 1.5 \text{ mol}$$

$$\text{total gaseous moles} = 0.25 + 0.75 + 1.5$$

$$= 2.5 \text{ mol}$$

$$p = \frac{nRT}{V} = \frac{2.5 \times 0.08 \times 300}{12} = 5 \text{ atm}$$

**Ex.17.** In the parallel radioactive decay,



the time when number of radioactive nuclei of A, B & C becomes equal is

[Given  $\lambda_1 = \ln 3 \text{ hr}^{-1}$ ,  $\lambda_2 = \ln 3 \text{ hr}^{-1}$ ]

(1) 0.5 min

(2) 30 min

(3) 60 min

(4) 90 min

**Ex.17. Ans.(2)**

**Sol.**  $C_A = C_{A_0} - C_B - C_C$

$$x = C_{A_0} - x - x$$

$$\text{or } 3x = C_{A_0} \Rightarrow x = \frac{C_{A_0}}{3}$$

$$\therefore C_A = C_{A_0} e^{-(\lambda_1 + \lambda_2)t}$$

$$\text{or } \frac{C_{A_0}}{3} = C_{A_0} e^{-(\lambda_1 + \lambda_2)t}$$

$$\text{or } 3 = e^{(\lambda_1 + \lambda_2)t}$$

$$\text{or } t = \frac{\ln 3}{2 \ln 3} = \frac{1}{2} \text{ hr} = 30 \text{ min}$$

## 8. APPLICATION OF RADIOACTIVITY AND RADIO ISOTOPES

### 8.1 IN MEDICINE :

- |                                  |   |                                                  |
|----------------------------------|---|--------------------------------------------------|
| (i) Testing of blood circulation | — | $\text{Cr}^{57}$                                 |
| (ii) Brain tumour detecting      | — | $\text{Hg}^{203}$                                |
| (iii) Thyroid testing (cancer)   | — | $\text{I}^{131}$                                 |
| (iv) Cancer cure                 | — | $\text{Co}^{60}$                                 |
| (v) Blood cancer cure            | — | $\text{Au}^{189}, \text{Na}^{24}, \text{P}^{32}$ |

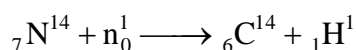
### 8.2 IN AGRICULTURE :

- |                                          |   |                  |
|------------------------------------------|---|------------------|
| (i) For protecting potato from earthworm | — | $\text{Co}^{60}$ |
| (ii) Fertilizers                         | — | $\text{P}^{32}$  |

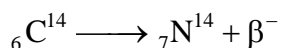
### 8.3 IN ARCHAEOLOGY :

#### 8.3.1 Carbon dating (age of fossils) :

Radiocarbon ( ${}_6\text{C}^{14}$ ) dating of historical wooden derived objects is based on the knowledge that the cosmic ray intensity (responsible for  $\text{C}^{14}$  production) has been practically constant for thousands of years.  $\text{C}^{14}$  is formed in the upper atmosphere by the action of cosmic radiation of  $\text{N}^{14}$ .



The  $C^{14}$  so produced is eventually converted into  $CO_2$ , which in turn is incorporated into plants and trees by the process of photosynthesis and then finds way into animals, which eat plants. Because of the natural plant-animal cycle, an equilibrium is set up and all living matter contains the same proportion of  $C^{14}$  as it occurs in the atmosphere. Once the plant or animal dies, the uptake of the  $CO_2$  by it ceases and the level of  $C^{14}$  in the dead begins to fall due to  $\beta^-$  decay.



A comparison of the  $\beta^-$ -activity of the dead matter with that of the carbon still in circulation enables measurement of the period of isolation of the material from the living cycle (age of fossil).

**Ex.18.** The beta activity of 1 g of carbon made from green wood is 15.3 counts per minute. If the activity of 1 g of carbon derived from the wood of an Egyptian mummy case is 9.4 counts per minute under the same conditions, how old is the wood of the mummy case?  $t_{1/2}$  of  $C^{14} = 5770$  yrs.

**Sol.**  $t = \frac{t_{1/2}}{\log 2} \cdot \log \frac{r_0}{r} = \frac{5770}{\log 2} \cdot \log \frac{15.3}{9.4} \approx 3920$  yrs.

### 8.3.2 Rock dating (Age of minerals, rocks, earth, etc) :

The age of the rocks and minerals may be determined by analysing the sample for a radionuclide (say  $U^{238}$ ) and its decay product ( $Pb^{206}$ ). Assuming that no decay product was present initially and all the intermediate products (if any) have achieved steady state, we can determine the age.

|                      |                       |               |
|----------------------|-----------------------|---------------|
|                      | $A \longrightarrow B$ |               |
|                      | radio nuclide         | decay product |
| $t = 0$              | a mole                | 0             |
| $t = \text{present}$ | (a-x) mole            | x mole        |

$\therefore$  age of rock,  $t = \frac{1}{\lambda} \ln \frac{a}{a-x}$

In the determination of age of earth, moon, etc, it is assumed that the rock was present from the time of evolution of earth, moon, etc.

**Ex.19.** A rock was found to contain  $U^{238}$  and  $Pb^{206}$  in 1.19: 1.03 mass ratio. What is the age of rock?  $t_{1/2}$  of  $U^{238} = 4.5 \times 10^9$  yrs.

**Sol.**

|         |                                    |                      |
|---------|------------------------------------|----------------------|
|         | $U^{238} \longrightarrow Pb^{206}$ |                      |
| $t = 0$ | a mole                             | 0                    |
| $t = t$ | (a-x) mole                         | x mole               |
|         | $= \frac{1.19}{238}$               | $= \frac{1.03}{206}$ |

$\therefore x = 5 \times 10^{-3}$  and  $a = 10 \times 10^{-3}$

Now,  $t = \frac{t_{1/2}}{\log 2} \cdot \log \frac{a}{a-x} = 4.5 \times 10^9$  yrs

**Ex.20.** To determine age of a stone it was analysed and  $10^{20}$  nuclei of A &  $7 \times 10^{20}$  nuclei of B were obtained. If nuclei B are assumed to be obtained only due to radioactive decay of A and no B was present initially. Find age of stone in days. [Half life of A = 1000 days]

**Sol.**  $A \longrightarrow B$

$$a - x = 10^{20} \quad x = 7 \times 10^{20}$$

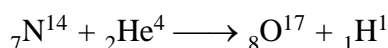
$$a = 10^{20} + 7 \times 10^{20} = 8 \times 10^{20}$$

$$\frac{a}{a-x} = \frac{8}{1}$$

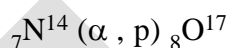
$$t = 3 \times t_{1/2} = 3 \times 1000 = 3000 \text{ days}$$

## 9. NUCLEAR REACTIONS

The reactions in which nuclei of atoms interact with other nuclei or elementary particles such as  $\alpha$ -particle, proton, neutron, deuteron, etc, resulting in the formation of new nuclei with or without liberation of one or more elementary particles, are called nuclear reactions. The particles causing nuclear reactions are also called projectiles. In all the nuclear reactions, the sum of number of protons and neutrons and the total charge are conserved. Nuclear reactions may be expressed as similar as chemical reactions, like



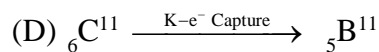
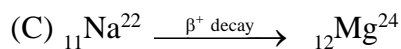
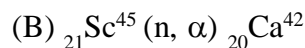
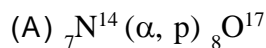
Here, the nucleus of nitrogen atom is converted in to the nucleus of oxygen atom by  $\alpha$ -particle and proton is also produced as a by-product. These reactions may be expressed by short hand notation, in which the projectile and the liberating particle are expressed by their symbols, in a small bracket in between the parent and the product nucleus. For example, the above reaction may also be expressed as :



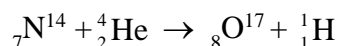
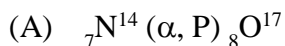
### 9.1 SOME DIFFERENCES BETWEEN NUCLEAR AND CHEMICAL REACTIONS :

| No. | Chemical reaction                                                                           | Nuclear reaction                                                                                      |
|-----|---------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------|
| 1.  | No new element is formed                                                                    | New element is formed                                                                                 |
| 2.  | Valence electrons of atoms participates                                                     | Only the nucleus of atoms participates                                                                |
| 3.  | Balanced by the conservation of atoms                                                       | Balanced by the conservation of nuclear charge and mass number (total number of neutrons and protons) |
| 4.  | Mass conservation is obeyed                                                                 | Disobey mass conservation                                                                             |
| 5.  | May be exothermic or endothermic, liberating or absorbing relatively small amount of energy | May be exothermic or endothermic, liberating or absorbing relatively very high amount of energy       |
| 6.  | May be reversible                                                                           | Irreversible                                                                                          |
| 7.  | May obey kinetics of any order                                                              | Obeys only first order kinetics                                                                       |
| 8.  | Rate depends on external factors like temperature and the catalytic conditions              | Rate is independent of any external condition                                                         |

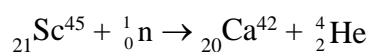
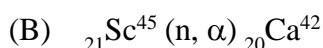
Ex.21. Select the incorrect nuclear reaction -



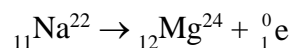
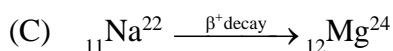
Ans (B, C)



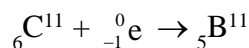
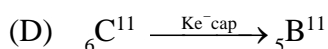
(A) is correct



(B) is incorrect



(C) is incorrect

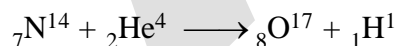


(D) is correct

hence Ans is (B) & (C)

## 9.2 ARTIFICIAL TRANSMUTATION :

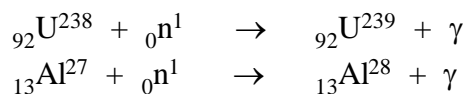
It is the method of conversion of atom of one element in to the atom of other element with the help of some particles like alpha particle, proton, deuteron, neutron, etc (called projectiles). The first such transmutation was performed by Rutherford. When  $\text{N}^{14}$  atoms were bombarded by very fast moving  $\alpha$ -particles, the nitrogen atom has changed in to oxygen atom and proton is produced simultaneously



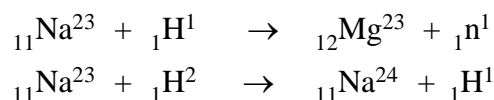
Later on, Rutherford and Chadwick showed that most of the nuclei may be transmuted by the suitable projectile. After the discovery of cyclotron, a particle accelerating machine, such transmutations became easier.

## 9.3 TYPES OF NUCLEAR REACTIONS :

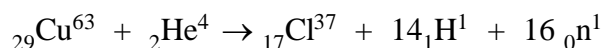
## (A) Projectile Capture Reactions :



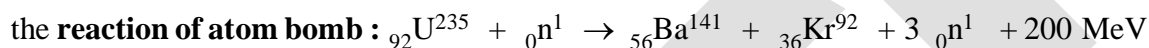
## (B) Particle - particle reactions :



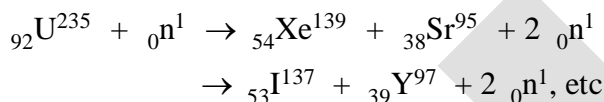
## (C) Spallation reactions : High speed projectiles with 400MeV bombarded on high nucleus giving smaller nucleus.



## (D) Fission reactions : It is the nuclear reaction in which a heavy nucleus is broken down by a slow or thermal neutron (energy about 0.04 eV) into two relatively smaller nuclei with the emission of two or more neutrons and large amount of energy. For example,

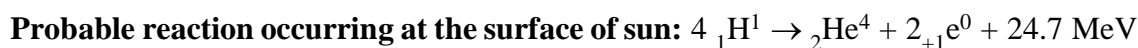


It is also found that the products of nuclear fission reactions are not unique. Some more products are formed. The most probable mass numbers of the two nuclides formed are around 95 and 140 and an average of 2.5 neutrons is emitted out per fission.



The destructive action of atom bomb is due to the following reasons:

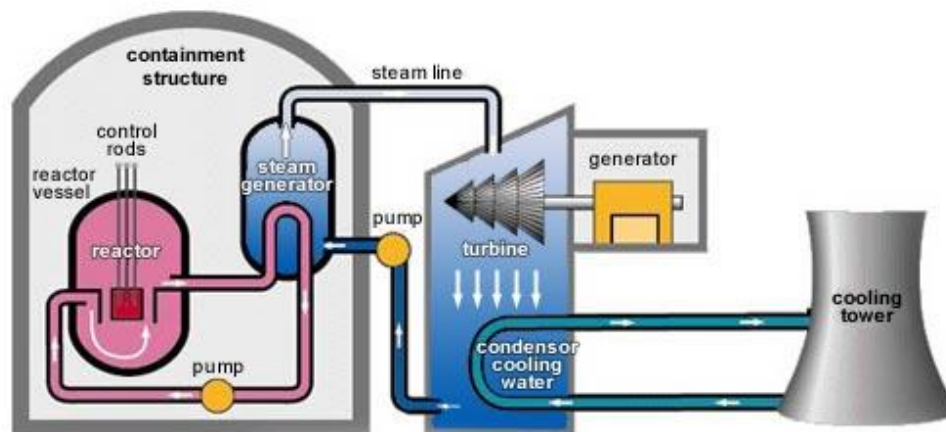
- (i) As some neutrons are produced in each fission, they may collide efficiently with the other  $\text{U}^{235}$  nuclei to produce more neutrons and thus the reaction occurs in chain like fashion. It results the emission of a large amount of energy in very small time.
- (ii) Each product of fission is radioactive and hence increases the intensity of radiation in that region, causing the problems due to radiations.

(E) Fusion reactions: It is the nuclear reaction in which two or more light nuclei fused together to form heavier nuclei, with the evolution of tremendous amount of energy. In such reactions, relatively more stable nucleus having higher binding energy per nucleon is formed. Such reaction is difficult to occur because when the nuclei of different atoms come closer, they repel each other strongly. This is why, very high temperature of the order  $10^6\text{K}$  is needed for the occurrence of such reactions. However, the overall reaction is highly exothermic due to large mass defect. Some examples of nuclear fusion reactions are :



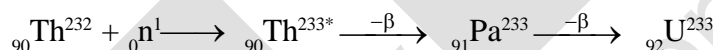
## 10. NUCLEAR REACTOR

A nuclear reactor is the furnace, place where nuclear fission reaction is performed to get energy. The essentials of a nuclear reactor are:



(A) **Fuel** : Nuclear fuels are of two types:

- (i) **Fissile materials** : These are the nuclides which directly results chain reaction on bombardment with slow neutrons. Such nuclides are  $U^{235}$ ,  $Pu^{239}$ ,  $U^{233}$ , etc.
- (ii) **Fertile material** : These are the nuclides which are non-fissile, but they may be converted in to a fissile material by the action of neutrons. Such nuclides are  $U^{238}$  and  $Th^{232}$ .



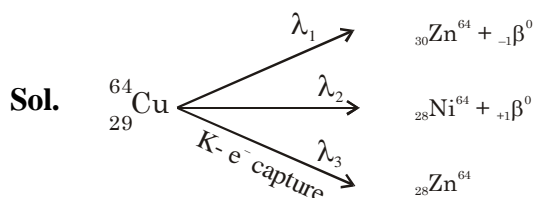
Such conversions are performed in a special type of nuclear reactor called **Breeder Reactor**.

- (B) **Moderator**: It is used to slow down the fast neutrons without absorbing them. Example: water, graphite, helium,  $D_2O$  etc.
- (C) **Control rods**: These are the rods of material which can absorb neutrons and hence control the fission reaction. Example: Cadmium, boron, etc.
- (D) **Coolant** : These are the material which transforms the energy produced in the fission reaction in to heat energy. Example: Liquid alloy of sodium and potassium, heavy water, polyphenyls, etc

## PREVIOUS MISCELLANEOUS QUESTION

Q.1  $^{64}\text{Cu}$  (half-life = 12.8 hr) decays by  $\beta^-$  emission (38%),  $\beta^+$  emission (19%) and electron capture (43%). Write the decay product and calculate partial half-lives for each of the decay processes. [JEE 2002]

Ans.  $^{64}_{30}\text{Zn}$ ,  $^{64}_{28}\text{Ni}$ ,  $(t_{1/2})_1 = 33.68$  hr,  $(t_{1/2})_2 = 67.36$  hr,  $(t_{1/2})_3 = 29.76$  hr



$$\frac{\lambda_1}{\lambda_1 + \lambda_2 + \lambda_3} \times 100 = 38 \quad \text{.....(i)}$$

$$\frac{\lambda_2}{\lambda_1 + \lambda_2 + \lambda_3} \times 100 = 18 \quad \text{.....(ii)}$$

$$\frac{\ln 2}{\lambda_1 + \lambda_2 + \lambda_3} = 12.8 \quad \text{.....(iii)}$$

On solving equations :

$$\lambda_1 = 0.38 \quad (t_{1/2})_I = 33.68 \text{ hr} ; (t_{1/2})_{II} = 67.36 ; (t_{1/2})_{III} = 29.7 \text{ hr}$$

Q.2 A radioactive sample emits  $n$   $\beta$ -particles in 2 sec. In next 2 sec it emits  $0.75n$   $\beta$ -particles, what is the mean life of the sample? [JEE 2003]

Ans.  $1.75n = N_0(1 - e^{-4\lambda})$ , 6.95 sec,  $\frac{2}{\ln\left(\frac{4}{3}\right)}$

Sol.  $n = N_0[1 - e^{-2\lambda}] \quad \text{.....(i)}$

$1.75n = N_0[1 - e^{-4\lambda}] \quad \text{.....(ii)}$

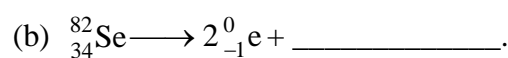
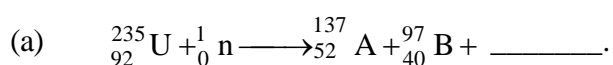
$\Rightarrow 1.75 = 1 + e^{-2\lambda}$

$$\frac{3}{4} = e^{-2\lambda}$$

$$\lambda = \frac{1}{2} \ln\left(\frac{4}{3}\right)$$

Q.3 Fill in the blanks

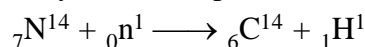
[JEE 2005]



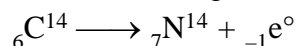
Ans. (a)  $2 {}^1_0\text{n}$ , (b)  $^{82}_{36}\text{Kr}$

## Question No. 4 to 6 (3 questions)

Carbon 14 is used to determine the age of organic material. The procedure is based on the formation of  $^{14}\text{C}$  by neutron capture in the upper atmosphere.



$^{14}\text{C}$  is absorbed by living organisms during photosynthesis. The  $^{14}\text{C}$  content is constant in living organism once the plant or animal dies, the uptake of carbon dioxide by it ceases and the level of  $^{14}\text{C}$  in the dead being falls due to the decay which  $\text{C}^{14}$  undergoes.



The half life period of  $^{14}\text{C}$  is 5770 years. The decay constant ( $\lambda$ ) can be calculated by using the

following formula  $\lambda = \frac{0.693}{t_{1/2}}$

The comparison of the  $\beta^-$  activity of the dead matter with that of carbon still in circulation enables measurement of the period of the isolation of the material from the living cycle. The method however, ceases to be accurate over periods longer than 30,000 years. The proportion of  $^{14}\text{C}$  to  $^{12}\text{C}$  in living matter is 1 :  $10^{12}$

[JEE 2006]

Q.4 Which of the following option is correct ?

- (A) In living organisms, circulation of  $^{14}\text{C}$  from atmosphere is high so the carbon content is constant in organism
- (B) Carbon dating can be used to find out the age of earth crust and rocks
- (C) Radioactive absorption due to cosmic radiation is equal to the rate of radioactive decay, hence the carbon content remains constant in living organism
- (D) Carbon dating cannot be used to determine concentration of  $^{14}\text{C}$  in dead beings.

Ans. (C)

Q.5 What should be the age of fossil for meaningful determination of its age?

- (A) 6 years
- (B) 6000 years
- (C) 60000 years
- (D) it can be used to calculate any age

Ans. (B)

Q.6 A nuclear explosion has taken place leading to increase in concentration of  $\text{C}^{14}$  in nearby areas.  $\text{C}^{14}$  concentration is  $C_1$  in nearby areas and  $C_2$  in areas far away. If the age of the fossil is determined to be  $t_1$  and  $t_2$  at the places respectively, then

(A) The age of the fossil will increase at the place where explosion has taken place and

$$t_1 - t_2 = \frac{1}{\lambda} \ln \frac{C_1}{C_2}$$

(B) The age of the fossil will decrease at the place where explosion has taken place and

$$t_1 - t_2 = \frac{1}{\lambda} \ln \frac{C_1}{C_2}$$

(C) The age of fossil will be determined to be the same

$$(D) \frac{t_1}{t_2} = \frac{C_1}{C_2}$$

Ans. (A)

**Sol.** Age in nearby areas :

$$\lambda t_1 = \ln \frac{C_1}{C_t} \dots\dots(i)$$

age in for away area

$$\lambda t_2 = \ln \frac{C_2}{C_t} \dots\dots(ii)$$

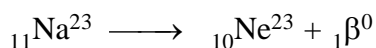
as  $C_1 > C_2$  so age of fossil increase is nearby areas by value.

$$(t_1 - t_2) = \frac{1}{\lambda} \ln \left( \frac{C_1}{C_2} \right)$$

**Q.7** A positron is emitted from  ${}^{23}_{11}\text{Na}$ . The ratio of the atomic mass and atomic number of the resulting nuclide is **[JEE 2006]**

- (A) 22/10 (B) 22/11 (C) 23/10 (D) 23/12

**Ans.** (C)



$$\frac{n}{p} = \frac{23}{10}$$

**Q.8** **STATEMENT-1 :** The plot of atomic number (y-axis) versus number of neutrons (x-axis) for stable nuclei shows a curvature towards x-axis from the line of  $45^\circ$  slope as the atomic number is increased.

**and**

**STATEMENT-2 :** Proton-proton electrostatic repulsions begin to overcome attractive forces involving protons and neutrons in heavier nuclides. **[JEE 2008]**

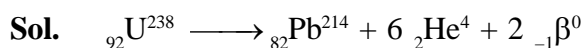
- (A) STATEMENT-1 is True, STATEMENT-2 is True ; STATEMENT-2 is a correct explanation for STATEMENT-1  
 (B) STATEMENT-1 is True, STATEMENT-2 is True ; STATEMENT-2 is NOT a correct explanation for STATEMENT-1  
 (C) STATEMENT-1 is True, STATEMENT-2 is False  
 (D) STATEMENT-1 is False, STATEMENT-2 is True

**Ans.** (A)

**Q.9** The total number of  $\alpha$  and  $\beta$  particles emitted in the nuclear reaction  ${}^{238}_{92}\text{U} \rightarrow {}^{214}_{82}\text{Pb}$  is.

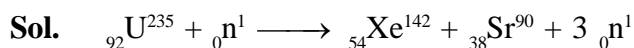
**[JEE 2009]**

**Ans.** (8)



**Q.10** The number of neutrons emitted when  ${}^{235}_{92}\text{U}$  undergoes controlled nuclear fission to  ${}^{142}_{54}\text{Xe}$  and  ${}^{90}_{38}\text{Sr}$  is - **[JEE 2010]**

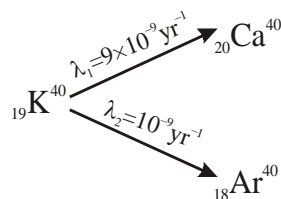
**Ans.** (4)



## EXERCISE (S-1)

- Q.1 Of the three isobars  $^{114}_{48}\text{Cd}$ ,  $^{114}_{49}\text{In}$  and  $^{114}_{50}\text{Sn}$ , which is likely to be radioactive? Explain your choice.
- Q.2 Classify each of the following nuclides as "beta ( $_{-1}^0\beta$ ) emitter", or "positron ( $_{+1}^0\beta$ ) emitter":  
 $^{49}_{20}\text{Ca}$ ,  $^{195}_{80}\text{Hg}$ ,  $^8_5\text{B}$ ,  $^{150}_{67}\text{Ho}$ ,  $^{30}_{13}\text{Al}$ ,  $^{94}_{36}\text{Kr}$ . Note:  $^{84}_{36}\text{Kr}$ ,  $^{200}_{80}\text{Hg}$  and  $^{165}_{67}\text{Ho}$  are stable
- Q.3 (a) Calculate number of  $\alpha$  and  $\beta$ -particles emitted when  $^{238}_{92}\text{U}$  changes into radioactive  $^{206}_{82}\text{Pb}$ .  
 (b)  $^{235}_{92}\text{U}$  disintegrates and emits  $4\beta$ - and  $7\alpha$ -particles to form a stable element. Find the atomic number and mass number of the stable product. Also identify the element.
- Q.4 A radioactive isotope disintegrates and emits  $6\beta$  and  $7\alpha$  particles to form a stable product. Find the difference between atomic number of parent radioactive isotope and the stable product.
- Q.5 Find the  $\alpha$ -activity of 1 gm  $^{200}\text{Ra}$ . ( $\lambda = 4.8 \times 10^{-7} \text{ min}^{-1}$ ) in dpm. ( $N_A = 6 \times 10^{23}$ )
- Q.6 The half life of the nuclide  $\text{Rn}^{220}$  is 54.5 sec. Find mass (in kg) of radon is equivalent to 1 millicurie.
- Q.7 At any given time a piece of radioactive material ( $t_{1/2} = 30$  days) contains  $10^{12}$  atoms. Calculate the activity of the sample in dps.
- Q.8 The activity of the radioactive sample drops to  $1/64$  of its original value in 2 hr. Find the decay constant ( $\lambda$ ).
- Q.9 A radioactive substance decays 20% in 10 min. If at start there are  $5 \times 10^{20}$  atoms present, find time after which the number of atoms will be reduced to  $10^{18}$ . ( $\log 2 = 0.3$ )
- Q.10 The half life period of  $^{125}_{53}\text{I}$  is 60 days. What % of radioactivity would be present after 240 days.
- Q.11 The activity of a radioactive sample decreases to  $1/3$  of the original activity ( $A_0$ ) in a period of 9 years. After 9 years more, its activity is  $A_0/x$ . Find the value of  $x$ .
- Q.12 5 moles of a radio-active isotope  $^A_Z\text{X}(\text{s})$  were taken in a 24.6 litre vessel at 600K and the following decay started :  $^A_Z\text{X}(\text{s}) \longrightarrow ^{A-8}_{Z-4}\text{Y}(\text{s})$
- If pressure developed after 16 hours was 15 atm, calculate half life of sample 'X' in hours.  
 Use :  $R = 0.082 \text{ L-atm/mol-K}$ .
- Q.13 Calculate the age of a vegetarian beverage whose tritium content is only 15% of the level in living plants. Given  $t_{1/2}$  for  $^3_1\text{H}$  = 12.3 years. ( $\log 2 = 0.3$ ,  $\log 3 = 0.48$ )
- Q.14 The volume of the blood in a patient is estimated by recording the activity of  $\text{Na}^{24}$  administered into the patient's blood. Find the volume (in  $\ell$ ) of the blood if the activity after 25 hrs is  $8 \text{ dpm m}^{-1}$ . Given the initial activity of  $\text{Na}^{24}$  sample is  $2 \times 10^3 \text{ Bq}$  when administered & the  $t_{1/2}$  for  $\text{Na}^{24} = 15$  hrs. (use  $32^{1/3} \approx 3$ )
- Q.15 A sample of  $\text{U}^{238}$  (half life =  $4.5 \times 10^9$  yr) ore is found to contain 23.8 g of  $\text{U}^{238}$  and 20.6 g of  $\text{Pb}^{206}$ . Calculate the age of the ore.
- Q.16 An isotopes of Potassium  $^{40}_{19}\text{K}$  has a half life of  $1.4 \times 10^9$  year and decays to Argon  $^{40}_{18}\text{Ar}$  which is stable.
- (i) Write down the nuclear reaction representing this decay.
- (ii) A sample of rock taken from the moon contains both potassium and argon in the ratio  $1/3$ . Find age of rock.

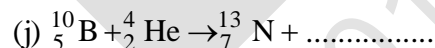
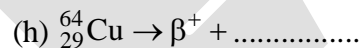
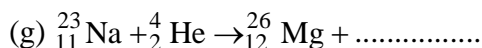
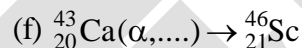
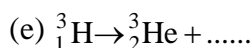
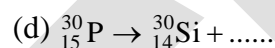
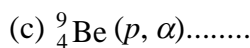
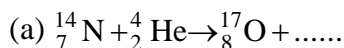
Q.17  $K^{40}$  decays into  $Ca^{40}$  &  $Ar^{40}$  simultaneously as follows



Ratio of atoms of 'Ar' to 'K' in a rock sample is 3 : 10. Calculate age of rock sample assuming that source of 'Ar' is radioactive decay of ' $K^{40}$ ' only and no 'Ar' was present at the time of formation of rock.

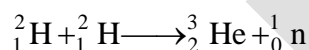
**If your answer is  $(\ln x) \times 10^8$  years, then the value of 'x' is.**

Q.18 Complete the following nuclear equations:



Q.19 Consider the following reaction;  ${}^2_1\text{H} + {}^2_1\text{H} \rightarrow {}^4_2\text{He} + Q$  : Mass of the deuterium atom = 2.0141 u ; Mass of the helium atom = 4.0024 u. Find approximate value of 'Q' (in MeV)

Q.20 Calculate the energy released in MeV in the following nuclear reaction:



Assume that the masses of  ${}^2_1\text{H}$ ,  ${}^3_2\text{He}$  and neutron (n) respectively are 2.020, 3.016 and 1.008 in amu.

### EXERCISE (S-2)

- Q.1 In the nuclear reaction  $X^{200} \longrightarrow A^{110} + B^{90}$ . If the binding energy per nucleon for X, A and B is 7.4 MeV, 8.2 MeV and 8.2 MeV respectively, Find the energy released.
- Q.2 The binding energies per nucleon for  ${}_1\text{H}^2$  and  ${}_2\text{He}^4$  are 1.1 MeV and 7.0 MeV respectively. Find the energy released when two deuterons fuse to form a helium nucleus.
- Q.3 When  ${}_c^a\text{X}$  changes to  ${}_d^b\text{Y}$ . Find number of  $\alpha$  and  $\beta$  particle.
- Q.4 At a given instant there are 25 % undecayed radioactive nuclei in a sample. After 10 sec, the number of undecayed nuclei remains 12.5 % . Calculate :

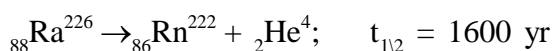
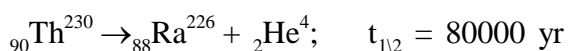
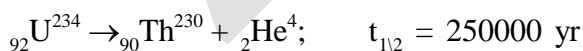
(i) mean – life of the nuclei and

(ii) The time in which the number of undecayed nuclear will further reduce to 6.25 % of the reduced number.

- Q.5 One of the hazards of nuclear explosion is the generation of  $\text{Sr}^{90}$  and its subsequent incorporation in bones. This nuclide has a half life of 40 year. Suppose one microgram was absorbed by a new-born child, how much  $\text{Sr}^{90}$  will remain in his bones after 20 years?
- Q.6 During the decay of 928 gm  ${}_{90}\text{Th}^{232}$  to  ${}_{82}\text{Pb}^{208}$ , total  $9.3 \times 10^{24}$   $\beta$ -particle are emitted upto 't' time. Then calculate t/T.

$$[\lambda \text{ of "Th"} = \frac{\ln 2}{T} ; N_A = 6 \times 10^{23}].$$

- Q.7 The  $\beta$  count given by carbon obtained from an ancient fossil was 12 counts per second, while the  $\beta$ -count given by carbon sample from freshly cut tree was found to be 15 count per second. What is the age of fossil in years. Given : ( $t_{1/2}$  of  $\text{C}^{14} = 5770$  yrs,  $\ln 5 = 1.6$ ,  $\ln 2 = 0.7$ )
- Q.8 The nuclidic ratio  ${}_1^3\text{H}$  to  ${}_1^1\text{H}$  in a sample of water is  $8.0 \times 10^{-18}$  : 1 Tritium undergoes decay with a half-life period of 12 years. How many tritium atoms would 10.0 g of such a sample contain 36 years after the original sample is collected.
- Q.9  $\text{Ac}^{227}$  has a half life of 22 year w.r.t radioactive decay. The decay follows two parallel paths, one leading the  $\text{Th}^{227}$  and the other leading to  $\text{Fr}^{223}$ . the percentage yields of these two daughters nucleides are 2% and 98% respectively. What is the rate constant in  $\text{yr}^{-1}$ , for each of the separate paths?
- Q.10. Consider the following process of decay,



After the above process has occurred for a long time, a state is reached where for every two thorium atoms formed from  ${}_{92}\text{U}^{234}$ , one decomposes to form  ${}_{88}\text{Ra}^{226}$  and for every two  ${}_{88}\text{Ra}^{226}$  formed, one decomposes. Calculate the ratio of number of atoms of  ${}_{90}\text{Th}^{230}$  to  ${}_{88}\text{Ra}^{226}$  at this state.

## EXERCISE (O-1)

- Q.1  ${}^{14}_6\text{C}$  decays by emission of  
 (A)  $\beta^-$  (B)  $\beta^+$  (C) n (D)  $\alpha$
- Q.2 When  ${}^{30}_{15}\text{P}$  emits a positron, the daughter nuclide formed is  
 (A)  ${}^{29}_{15}\text{P}$  (B)  ${}^{30}_{16}\text{Si}$  (C)  ${}^{30}_{14}\text{Si}$  (D)  ${}^{30}_{16}\text{P}$
- Q.3  ${}^{27}_{13}\text{Al}$  is a stable isotope.  ${}^{29}_{13}\text{Al}$  is expected to disintegrated by  
 (A)  $\alpha$  emission (B)  ${}^0_{-1}\beta$  emission (C) Positron emission (D) Proton emission
- Q.4 Loss of a  $\beta^-$  particle is equivalent to  
 (A) Increase of one proton only  
 (B) Decrease of one neutron only  
 (C) Increase of one proton and decrease of one neutron  
 (D) None of these.
- Q.5 Which of the following nuclear reactions will generate an isotope?  
 (A) neutron emission (B) positron emission  
 (C)  $\alpha$ -emission (D)  $\beta$ -emission
- Q.6 The  $\text{S}^{35}$  is neutron-rich, therefore, it is likely to undergo radioactive decay by  
 (A) electron capture (B) beta emission (C) positron emission (D) alpha emission
- Q.7 The number of  $\alpha$  and  $\beta$ -particles emitted, when the following nuclear transformation takes place are \_\_\_\_\_ and \_\_\_\_\_ respectively.  

$${}^{238}_{92}\text{X} \longrightarrow {}^{206}_{82}\text{Y}$$
  
 (A) 6, 2 (B) 5, 6 (C) 8, 4 (D) 8, 6
- Q.8  ${}^{88}_{35}\text{X}$  an unstable isotope, decays in two successive steps to produce stable isotope  ${}^{84}_{32}\text{Z}$  as  

$${}^{88}_{35}\text{X} \xrightarrow{\text{I}} \text{Y} \xrightarrow{\text{II}} {}^{84}_{32}\text{Z}$$
  
 The correct statement is (possible emission are  $\alpha$ ,  $\beta$ , positron, neutron, and K-capture)  
 (A) I may involve a  $\beta$ -emission. (B) II may involve a neutron emission  
 (C) Y and Z may be isodiaphers (D) X and Z may be isodiaphers
- Q.9 Which of the following can not be natural decay product (only  $\alpha$ ,  $\beta$  &  $\gamma$  decay) of  ${}^{232}_{90}\text{Th}$   
 (A)  ${}^{228}_{89}\text{Ac}$  (B)  ${}^{220}_{86}\text{Rn}$  (C)  ${}^{226}_{88}\text{Ra}$  (D)  ${}^{216}_{84}\text{Po}$
- Q.10 The half-life of a radioactive isotope is three hours. If the initial mass of the isotope were 256 g, the mass of it remaining undecayed after 18 hours would be  
 (A) 16.0 g (B) 4.0 g (C) 8.0 g (D) 12.0 g
- Q.11 The half-life of a radioisotope is four hours. If the initial rate of the isotope was 200 dpm, the rate after 24 hours is  
 (A) 6.25 dpm (B) 2.084 dpm (C) 3.125 dpm (D) 4.167 dpm



- Q.12 The half life of  $\text{Tc}^{99}$  is 6.0 hr. The delivery of a sample of  $\text{Tc}^{99}$  from the reactor to the nuclear medicine lab of a certain hospital takes 3.0 hr. What is the minimum amount of  $\text{Tc}^{99}$  that must be shipped in order for the lab to receive 10.0 mg? ( $\sqrt{2} = 1.41$ )  
 (A) 20.0 mg (B) 15.0 mg (C) 14.1 mg (D) 12.5 mg
- Q.13 Two radioactive nuclides A and B have half lives of 50 min and 10 min respectively. A fresh sample contains the nuclides of B to be eight time that of A. How much time should elapse so that the number of nuclides of A becomes double of B  
 (A) 30 min. (B) 40 min. (C) 50 min. (D) 100 min.
- Q.14 A radioactive sample had an initial activity of 56 dpm (disintegration per min). After 69.3 min it was found to have an activity of 28 dpm. Find the number of atoms in a sample having an activity of 10 dpm.  
 (A) 693 (B) 1000 (C) 100 (D) 10,000
- Q.15. The radioactivity of a sample is  $R_1$  at a time  $T_1$  and  $R_2$  at a time  $T_2$ . If the half life of the specimen is  $T$ , the number of atoms that have disintegrated in the time  $(T_2 - T_1)$  is equal to  
 (A)  $(R_1 T_1 - R_2 T_2)$  (B)  $(R_1 - R_2)$  (C)  $(R_1 - R_2) / T$  (D)  $(R_1 - R_2) T / 0.693$
- Q.16 The analysis of a mineral of uranium reveals that ratio of mole of  $^{206}\text{Pb}$  and  $^{238}\text{U}$  in sample is 0.2. If effective decay constant of process  $^{238}\text{U} \longrightarrow ^{206}\text{Pb}$  is  $\lambda$  then age of rock is  
 (A)  $\frac{1}{\lambda} \ln \left( \frac{5}{4} \right)$  (B)  $\frac{1}{\lambda} \ln \left( \frac{5}{1} \right)$  (C)  $\frac{1}{\lambda} \ln \left( \frac{4}{1} \right)$  (D)  $\frac{1}{\lambda} \ln \left( \frac{6}{5} \right)$
- Q.17 Wooden article and freshly cut tree show activity of 7.6 and 15.2  $\text{min}^{-1} \text{gm}^{-1}$  of carbon ( $t_{1/2} = 5760$  years) respectively. The age of article in years, is  
 (A) 5760 (B)  $5760 \times \left( \frac{15.2}{7.6} \right)$  (C)  $5760 \times \left( \frac{7.6}{15.2} \right)$  (D)  $5760 \times (15.2 - 7.6)$
- Q.18 Symbol is needed to complete the nuclear equation  $^{63}_{29}\text{Cu}(p, \dots) ^{62}_{29}\text{Cu}$   
 (A)  $^1_1\text{H}^2$  (B)  $^1_0\text{n}^1$  (C)  $^4_2\text{He}^4$  (D)  $^0_{-1}\text{n}^0$
- Q.19 Consider the following nuclear reactions:  
 $^{238}_{92}\text{M} \rightarrow ^X_Y\text{N} + 2\ ^4_2\text{He};$   
 $^X_Y\text{N} \rightarrow ^A_B\text{L} + 2\beta^+$   
 The number of neutrons in the element L is  
 (A) 142 (B) 144 (C) 140 (D) 146
- Q.20 The number of neutrons accompanying the formation of  $^{139}_{54}\text{X}$  and  $^{94}_{38}\text{Sr}$  from the absorption of slow neutron by  $^{235}_{92}\text{U}$  followed by nuclear fission is  
 (A) 0 (B) 2 (C) 1 (D) 3

## EXERCISE (O-2)

- Q.1 Helium nuclei combines to form an oxygen nucleus. The energy released per nucleon of oxygen nucleus is if  $m_0 = 15.834$  amu and  $m_{\text{He}} = 4.0026$  amu  
(A) 10.27 MeV (B) 0 MeV (C) 5.24 MeV (D) 164.3 MeV
- Q.2 A radioactive element gets spilled over the floor of a room. Its half-life period is 30 days. If the initial activity is ten times the permissible value, after how many minimum days will it be safe to enter the room?  
(A) 1000 days (B) 300 days (C) 10 days (D) 100 days
- Q.3 The radioactive sources A and B of half lives of  $t$  hr and  $2t$  hr respectively, initially contain the same number of radioactive atoms. At the end of  $t$  hours, their rates of disintegration are in the ratio :  
(A)  $2\sqrt{2} : 1$  (B)  $1 : 8$  (C)  $\sqrt{2} : 1$  (D)  $1 : \sqrt{2}$
- Q.4 The average (mean) life at a radio nuclide which decays by parallel path is  
 $A \xrightarrow{\lambda_1} B; \quad \lambda_1 = 1.8 \times 10^{-2} \text{ sec}^{-1}$   
 $A \xrightarrow{\lambda_2} C; \quad \lambda_2 = 2 \times 10^{-3} \text{ sec}^{-1}$   
 (A) 52.63 sec (B) 500 sec (C) 50 sec (D) None
- Q.5 A sample of  $^{14}\text{CO}_2$  was to be mixed with ordinary  $\text{CO}_2$  for a biological tracer experiment. In order that  $10 \text{ cm}^3$  of diluted gas at STP should have  $10^4$  dis/min, what activity (in  $\mu\text{Ci}$ ) of radioactive carbon is needed to prepare 60 L of diluted gas at STP. [ $1 \text{ Ci} = 3.7 \times 10^{10} \text{ dps}$ ]  
(A) 270  $\mu\text{Ci}$  (B) 27  $\mu\text{Ci}$  (C) 2.7  $\mu\text{Ci}$  (D) 2700  $\mu\text{Ci}$

**Multiple correct :**

- Q.6 Select **correct** statement(s):  
 (A) The emission of gamma radiation involves transition between energy levels within the nucleus.  
 (B)  $^4_2\text{He}$  is formed due to emission of beta particle from tritium  $^3_1\text{H}$ .  
 (C) When positron ( $^0_{+1}\text{e}$ ) is emitted,  $\frac{n}{p}$  ratio increases.  
 (D) Decay constant of radioactive substance is independent of temperature.
- Q.7 Select the correct statements  
 (A) A radioactive element decays by emitting one  $\alpha$  and two  $\beta$ -particles. The daughter element formed is an isotope of the parent element.  
 (B) The daughter product formed by the emission of  $\alpha$ -particle has mass number less by 4 units than the parent nuclide.  
 (C)  $^{27}_{13}\text{Al}$  is a stable isotope hence  $^{29}_{13}\text{Al}$  is expected to disintegrate by  $\beta$ -emission.  
 (D) Emission of a  $\beta$ -particle by a radioactive nuclide results in decrease in  $n/p$  ratio.
- Q.8 Select the correct statements  
 (A) The decay constant of the end product of a radioactive series is zero  
 (B) Positron has same mass as that of an electron.  
 (C)  $^{14}_9\text{N}$  and  $^{16}_8\text{O}$  are isotones.  
 (D) The S.I. unit of activity is Curie (Ci).

Q.9 Select the correct statements

- (A) Half-life period of a radioactive substance can be changed by using some suitable catalyst.
- (B) The nuclides with same difference of number of neutrons and number of protons are called isodiaphers
- (C) Half life for certain radioactive element is 15 min. Four nuclei of that element are observed at a certain instant of time. After fifteen minutes, it can be definitely said that two nuclei will be left undecayed.
- (D)  $5\alpha$  and  $4\beta^-$  are emitted during the radioactive decay chain starting from  ${}^{226}_{88}\text{Ra}$  and ending at  ${}^{206}_{82}\text{Pb}$

Q.10 Select the correct statement(s) -

- (A)  ${}_{15}\text{P}^{29}$  may emit positron to increase n / p ratio
- (B) During  $\beta^-$  emission, neutron changes into proton in nucleus
- (C) Energy liberated during nuclear fission or fusion is mainly due to mass defect
- (D) Binding energy per nucleon increases continuously with mass number

### Assertion & Reason

Q.11. **Statement-1** :  ${}^{238}\text{UF}_6$  and  ${}^{238}\text{U}$  both have same specific activity.

**Statement-2** :  ${}^{238}\text{U}$  has same half life whether in free state or bonded state.

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
- (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
- (C) Statement-1 is true, statement-2 is false.
- (D) Statement-1 is false, statement-2 is true.

Q.12. **Statement-1** : An element may belong to more than one disintegration series.

**Statement-2** : Mass number of an element decides the disintegration series to which it belongs.

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
- (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
- (C) Statement-1 is true, statement-2 is false.
- (D) Statement-1 is false, statement-2 is true.

Q.13 **STATEMENT-1** : The plot of atomic number (y-axis) versus number of neutrons (x-axis) for stable nuclei shows a curvature towards x-axis from the line of  $45^\circ$  slope as the atomic number is increased.

**and**

**STATEMENT-2** : Proton-proton electrostatic repulsions begin to overcome attractive forces involving protons and neutrons in heavier nuclides.

[JEE 2008]

- (A) STATEMENT-1 is True, STATEMENT-2 is True ; STATEMENT-2 is a correct explanation for STATEMENT-1
- (B) STATEMENT-1 is True, STATEMENT-2 is True ; STATEMENT-2 is NOT a correct explanation for STATEMENT-1
- (C) STATEMENT-1 is True, STATEMENT-2 is False
- (D) STATEMENT-1 is False, STATEMENT-2 is True

☐ COMPREHENSION :

**Paragraph for Q.14 to 15**

Mass defect in the nuclear reactions may be expressed in terms of the atomic masses of the parent and daughter nuclides in place of their nuclear masses.

- Q.14 The mass defect of nuclear reaction:  ${}_4\text{Be}^{10} \rightarrow {}_5\text{B}^{10} + e^-$  is
- (A)  $\Delta m = \text{At. mass of } {}_4\text{Be}^{10} - \text{At. mass of } {}_5\text{B}^{10}$
- (B)  $\Delta m = \text{At. mass of } {}_4\text{Be}^{10} - \text{At. mass of } {}_5\text{B}^{10} - \text{mass of one electron}$
- (C)  $\Delta m = \text{At. mass of } {}_4\text{Be}^{10} - \text{At. mass of } {}_5\text{B}^{10} + \text{mass of one electron}$
- (D)  $\Delta m = \text{At. mass of } {}_4\text{Be}^{10} - \text{At. mass of } {}_5\text{B}^{10} - \text{mass of two electrons}$

- Q.15 The mass defect of the nuclear reaction:  ${}_5\text{B}^8 \rightarrow {}_4\text{Be}^8 + e^+$  is
- (A)  $\Delta m = \text{At. mass of } {}_5\text{B}^8 - \text{At. mass of } {}_4\text{Be}^8$
- (B)  $\Delta m = \text{At. mass of } {}_5\text{B}^8 - \text{At. mass of } {}_4\text{Be}^8 - \text{mass of one electron}$
- (C)  $\Delta m = \text{At. mass of } {}_5\text{B}^8 - \text{At. mass of } {}_4\text{Be}^8 + \text{mass of one electron}$
- (D)  $\Delta m = \text{At. mass of } {}_5\text{B}^8 - \text{At. mass of } {}_4\text{Be}^8 - \text{mass of two electrons}$

- Q.16 **Match the Column-I with Column-II**

**Column-I**

- (A)  ${}_1^2\text{D} + {}_1^3\text{T} \rightarrow {}_2^4\text{He} + {}_0^1\text{n} + \text{energy}$
- (B)  ${}_4^9\text{Be} + {}_2^4\text{He} \rightarrow {}_6^{12}\text{C} + {}_0^1\text{n}$
- (C)  ${}_{12}^{24}\text{Mg} + {}_2^4\text{He} \rightarrow {}_{14}^{27}\text{Si} + {}_0^1\text{n}$
- (D)  ${}_0^1\text{n} \longrightarrow {}_1^1\text{H} + {}_{-1}^0\text{e}$

**Column-II**

- (P)  $\beta$ -emission
- (Q) Artificial transmutation
- (R) Discovery of neutrons
- (S) Hydrogen bomb

- Q.17

**Column-I**

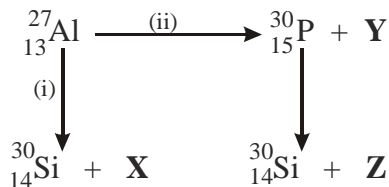
- (A)  $\text{n} \longrightarrow \text{p} + \dots\dots\dots$
- (B)  $\text{p} \longrightarrow \text{n} + \dots\dots\dots$
- (C) X-ray emission
- (D)  $4[{}_1^1\text{H}] \longrightarrow \dots\dots + 2\beta^+ + \text{energy}$

**Column-II**

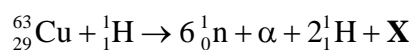
- (P) Positron emission
- (Q)  $\beta$ -emission
- (R) K-electron capture
- (S)  $\alpha$ -emission

EXERCISE : J-ADVANCED

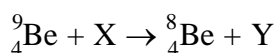
- Q.1 Bombardment of aluminium by  $\alpha$ -particle leads to its artificial disintegration in two ways, (i) and (ii) as shown. Products **X**, **Y** and **Z** respectively are : [JEE 2011]



- (A) proton, neutron, positron  
(B) neutron, positron, proton  
(C) proton, positron, neutron  
(D) positron, proton, neutron
- Q.2 The periodic table consists of 18 groups. An isotope of copper, on bombardment with protons, undergoes a nuclear reaction yielding element **X** as shown below. To which group, element **X** belongs in the periodic table ? [JEE 2012]



- Q.3 In the nuclear transmutation [JEE 2013]



(X, Y) is(are)

- (A) ( $\gamma$ , n) (B) (p, D) (C) (n, D) (D) ( $\gamma$ , D)
- Q.4 A closed vessel with rigid walls contains 1 mol of  ${}^{238}_{92}\text{U}$  and 1 mol of air at 298 K. Considering complete decay of  ${}^{238}_{92}\text{U}$  to  ${}^{206}_{82}\text{Pb}$ , the ratio of the final pressure to the initial pressure of the system at 298 K is - [JEE 2015]
- Q.5 A plot of the number of neutrons (N) against the number of protons (P) of stable nuclei exhibits upwards deviation from linearity for atomic number,  $Z > 20$ . For an unstable nucleus having N/P ratio less than 1, the possible mode(s) of decay is(are) - [JEE 2016]
- (A)  $\beta^-$  decay ( $\beta$  emission) (B) orbital or K-electron capture  
(C) Neutron emission (D)  $\beta^+$  decay (positron emission)

**ANSWER KEY****EXERCISE (S-1)**

- Q.1 Ans.  $^{114}_{49}\text{In}$ , odd number of nucleons
- Q.2 Ans. beta emitter :  $^{49}\text{Ca}$ ,  $^{30}\text{Al}$ ,  $^{94}\text{Kr}$ , positron emitter :  $^{195}\text{Hg}$ ,  $^8\text{B}$ ,  $^{150}\text{Ho}$
- Q.3. Ans. (a) No. of  $\alpha$ -particles = 8, No. of  $\beta$ -particles = 6 ; (b)  $^{207}_{82}\text{Pb}$
- Q.4 Ans. (8) Q.5 Ans.  $1.44 \times 10^{15}$  dpm.
- Q.6 Ans.  $1.06 \times 10^{-15}$  Q.7 Ans.  $2.67 \times 10^5$  dps
- Q.8 Ans.  $\lambda = 2.079 \text{ hr}^{-1}$  Q.9 Ans. 4.5 hr
- Q.10 Ans. 6.25 % Q.11 Ans. 9
- Q.12 Ans. (8) Q.13 Ans. 33.62 years
- Q.14 Ans.(5) Q.15 Ans.  $4.5 \times 10^9$  year
- Q.16 Ans. (i)  $^{40}_{19}\text{K} \longrightarrow ^{40}_{18}\text{Ar} + ^0_{+1}\beta + \nu$  (ii)  $2.8 \times 10^9$  years
- Q.17 Ans (4)
- Q.18 (a)  $^1_1\text{H}$ , (b)  $^1_0\text{n}$ , (c)  $^6_3\text{Li}$ , (d)  $^0_{+1}\text{e}$ , (e)  $^0_{-1}\text{e}$ , (f) p (proton)  
 (g)  $^1_1\text{H}^1$  (h)  $^{64}_{28}\text{Ni}$  (i)  $^0_{-1}\text{e}$  (j)  $^1_0\text{n}$
- Q.19 Ans. 24
- Q.20 Ans.  $\Delta E = 14.904 \text{ MeV}$

**EXERCISE (S-2)**

- Q.1 Ans. 160 MeV.
- Q.2 Ans. 23.6 MeV
- Q.3 Ans.  $\alpha = \frac{a-b}{4}$ ;  $\beta = d + \frac{(a-b)}{2} - c$
- Q.4 Ans. (i)  $t_{\text{means}} = 14.43 \text{ s}$  (ii) 40 seconds
- Q.5 Ans.  $7.07 \times 10^{-7} \text{ gm}$
- Q.6 Ans. (5)
- Q.7 Ans. 1648.6
- Q.8 Ans.  $6.67 \times 10^5$
- Q.9 Ans. ( $6.30 \times 10^{-4} \text{ yr}^{-1}$ ,  $3.087 \times 10^{-2} \text{ yr}^{-1}$ )
- Q.10. Ans. 100

**EXERCISE (O-1)**

- |              |              |               |              |
|--------------|--------------|---------------|--------------|
| Q.1 Ans.(A)  | Q.2 Ans.(C)  | Q.3 Ans.(B)   | Q.4 Ans.(C)  |
| Q.5 Ans.(A)  | Q.6 Ans.(B)  | Q.7 Ans.(D)   | Q.8. Ans.(C) |
| Q.9 Ans.(C)  | Q.10 Ans.(B) | Q.11 Ans.(C)  | Q.12 Ans.(C) |
| Q.13 Ans.(C) | Q.14 Ans.(B) | Q.15. Ans.(D) | Q.16 Ans.(D) |
| Q.17 Ans.(A) | Q.18 Ans.(A) | Q.19 Ans.(B)  | Q.20 Ans.(D) |

**EXERCISE (O-2)**

|      |                                               |       |             |       |               |       |           |
|------|-----------------------------------------------|-------|-------------|-------|---------------|-------|-----------|
| Q.1  | Ans.(A)                                       | Q.2   | Ans.(D)     | Q.3   | Ans.(C)       | Q.4   | Ans.(C)   |
| Q.5  | Ans.(B)                                       | Q.6   | Ans.(A,C,D) | Q.7   | Ans.(A,B,C,D) | Q.8   | Ans.(A,B) |
| Q.9  | Ans.(B,D)                                     | Q.10. | Ans (A,B,C) | Q.11. | Ans.(D)       | Q.12. | Ans.(A)   |
| Q.13 | Ans.(A)                                       | Q.14  | Ans.(A)     | Q.15  | Ans.(D)       |       |           |
| Q.16 | Ans. (A) - S ; (B) - Q, R ; (C) - Q ; (D) - P |       |             |       |               |       |           |
| Q.17 | Ans. (A) - Q ; (B) - P ; (C) - R ; (D) - S    |       |             |       |               |       |           |

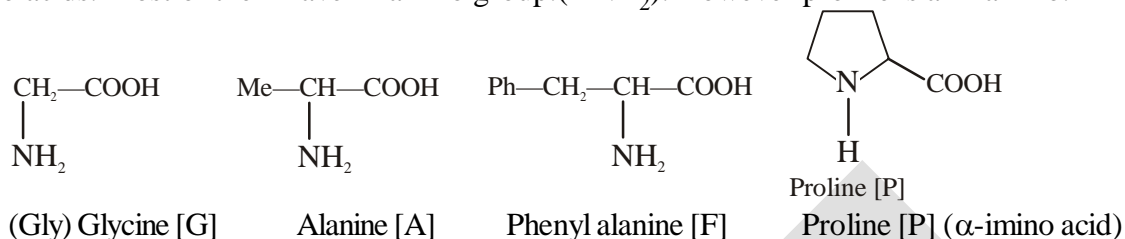
**EXERCISE (J-ADVANCED)**

|     |            |     |          |
|-----|------------|-----|----------|
| Q.1 | Ans. (A)   | Q.2 | Ans. (8) |
| Q.3 | Ans. (A,B) | Q.4 | Ans. (9) |
| Q.5 | Ans.(B, D) |     |          |

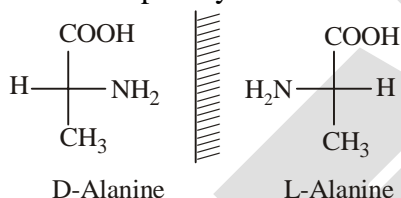
## AMINO ACIDS AND PROTEINS

Bifunctional compounds having an acidic carboxylic group & a basic amino group are known as amino acid.

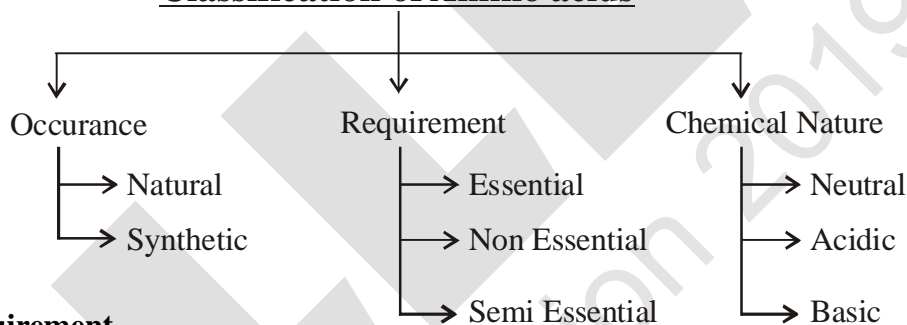
There are 20 amino acids commonly found in proteins and are standard amino acids. All are  $\alpha$  amino acids. Most of them have  $1^\circ$  amino group ( $-\text{NH}_2$ ). However proline is a  $2^\circ$  amino.



All amino acids are chiral molecules with at least one chiral carbon (except glycine,  $\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-$ ). Except Glycine all other amino acids are optically active & can be assigned D & L configuration.



### Classification of Amino acids



#### Based on requirement.

- Essential amino acids can not be synthesized in human body so dietary intake is required. For any human being 1 gm a day is required.
- Semi essential amino acids can be synthesized in human body but dietary intake is required during growing stages (when more of cell division is required).  
For example : Early childhood, pregnancy and lactating mother.
- Non essential amino acid - Body can synthesize them.

#### Based on chemical nature

**Neutral** - Amino acid having equal number of  $\text{NH}_2$  and  $\text{COOH}$ .

Neutral amino acids are further classified as polar and nonpolar depending on whether their side chains have polar substituents (for example, asparagine with an  $\text{NH}_2\text{CO}$  group) or are completely hydrocarbon in nature (for example alanine, valine etc.).

**Acidic** - Amino acid having more  $\text{COOH}$  than  $\text{NH}_2$  group.

For example : Aspartic acid and glutamic acids, each with a second  $\text{CO}_2\text{H}$  in their side chain are acidic amino acids.

**Basic** - Amino acid having more  $\text{NH}_2$  than  $\text{COOH}$  group.

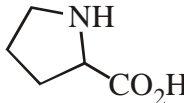
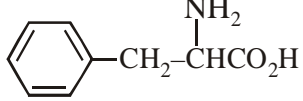
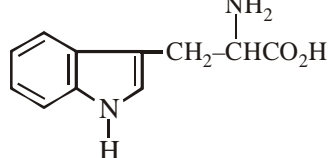
For example : Lysine, arginine and histidine)

**Proteins:** The name protein is taken from the Greek word "proteios", which means "first". Of all chemical compounds, proteins must almost certainly be ranked first, for they are the substance of life.

Proteins make up a large part of the animal body, they hold it together and they run it. They are found in all living cells.



Chemically, proteins are high polymers. They are polyamides and the monomers from which they are derived are the  $\alpha$  - amino carboxylic acids. A single protein molecule contains hundreds or even thousands of amino acid units. These units can be of twenty-odd different kinds. The number of different combinations, i.e., the number of different protein molecules that are possible, is almost infinite.

| <i>A -1. Neutral amino acids (with nonpolar side chains)</i> |               |                                                                                                                                                                                                                                            |                       |
|--------------------------------------------------------------|---------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| NAME                                                         | ABBREVIATIONS | STRUCTURAL FORMULAE                                                                                                                                                                                                                        | ISOELECTRIC POINT[pI] |
| @Glycine                                                     | Gly(G)        | $\begin{array}{c} \text{NH}_2 \\   \\ \text{H}_2\text{C} \\   \\ \text{C}=\text{O} \\   \\ \text{OH} \end{array}$                                                                                                                          | 6.0                   |
| Alanine                                                      | Ala(A)        | $\begin{array}{c} \text{NH}_2 \\   \\ \text{H}_3\text{C}-\text{CH} \\   \\ \text{C}=\text{O} \\   \\ \text{OH} \end{array}$                                                                                                                | 6.0                   |
| Valine*                                                      | Val(V)        | $\begin{array}{c} \text{H}_3\text{C}-\text{CH}-\text{C}-\text{NH}_2 \\   \quad \quad   \\ \text{CH}_3 \quad \quad \text{C}=\text{O} \\ \quad \quad \quad   \\ \quad \quad \quad \text{OH} \end{array}$                                     | 6.0                   |
| Leucine*                                                     | Leu(L)        | $\begin{array}{c} \text{H}_3\text{C}-\text{CH}-\text{CH}_2-\text{C}-\text{NH}_2 \\   \quad \quad \quad   \\ \text{CH}_3 \quad \quad \quad \text{C}=\text{O} \\ \quad \quad \quad \quad   \\ \quad \quad \quad \quad \text{OH} \end{array}$ | 6.0                   |
| Isoleucine*                                                  | Ile(I)        | $\begin{array}{c} \text{CH}_3 \quad \text{NH}_2 \\   \quad \quad   \\ \text{CH}_3\text{CH}_2\text{CH}-\text{CHCO}_2\text{H} \end{array}$                                                                                                   | 6.0                   |
| Methionine*                                                  | Met(M)        | $\begin{array}{c} \text{NH}_2 \\   \\ \text{CH}_3\text{SCH}_2\text{CH}-\text{CHCO}_2\text{H} \end{array}$                                                                                                                                  | 5.7                   |
| @@Proline                                                    | Pro(P)        |                                                                                                                                                        | 6.3                   |
| Phenylalanine*                                               | Phe(F)        |                                                                                                                                                        | 5.5                   |
| Tryptophan*                                                  | Trp(W)        |                                                                                                                                                        | 5.9                   |

**A -2. Neutral amino acids (with polar, but nonionized side chains)**

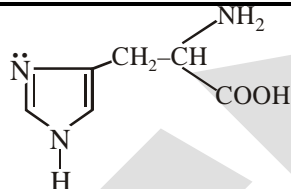
| NAME       | ABBREVIATIONS | STRUCTURAL FORMULAE                                                                                                                                                      | ISOELECTRIC POINT [pI] |
|------------|---------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------|
| Asparagine | Asn(N)        | $\text{H}_2\text{N}-\overset{\text{O}}{\underset{\text{  }}{\text{C}}}-\text{CH}_2-\underset{\text{C}=\text{O}}{\overset{\text{NH}_2}{\text{CH}}}-\text{OH}$             | 5.4                    |
| Glutamine  | Gln(Q)        | $\text{H}_2\text{N}-\overset{\text{O}}{\underset{\text{  }}{\text{C}}}-\text{CH}_2-\text{CH}_2-\underset{\text{C}=\text{O}}{\overset{\text{NH}_2}{\text{CH}}}-\text{OH}$ | 5.7                    |
| Serine     | Ser(S)        | $\text{HO}-\text{CH}_2-\underset{\text{C}=\text{O}}{\overset{\text{NH}_2}{\text{CH}}}-\text{OH}$                                                                         | 5.7                    |

**A -3. Neutral amino acids (with polar, but nonionized side chains)**

| NAME       | ABBREVIATIONS | STRUCTURAL FORMULAE                                                                                 | ISOELECTRIC POINT [pI] |
|------------|---------------|-----------------------------------------------------------------------------------------------------|------------------------|
| Threonine* | Thr           | $\text{CH}_3-\underset{\text{OH}}{\text{CH}}-\underset{\text{NH}_2}{\text{CH}}-\text{CO}_2\text{H}$ | 5.6                    |
| Tyrosine   | Tyr(Y)        | $\text{HO}-\text{C}_6\text{H}_4-\underset{\text{NH}_2}{\text{CH}}-\text{CO}_2\text{H}$              | 5.7                    |
| Cysteine   | Cys           | $\text{HSCH}_2-\underset{\text{NH}_2}{\text{CH}}-\text{CO}_2\text{H}$                               | 5.1                    |
| ± Cystine  | Cys-Cys       | $\text{HOOCCH}(\text{NH}_2)\text{CH}_2\text{S}-\text{SCH}_2\text{CH}(\text{NH}_2)\text{COOH}$       |                        |

**B - Acidic amino acids (side chain with carboxylic acid group)**

| NAME          | ABBREVIATIONS | STRUCTURAL FORMULAE                                                                                                                                                       | ISOELECTRIC POINT [pI] |
|---------------|---------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------|
| Aspartic acid | Asp(D)        | $\text{HO}-\overset{\text{O}}{\underset{\text{  }}{\text{C}}}-\text{CH}_2-\underset{\text{NH}_2}{\text{CH}}-\overset{\text{O}}{\underset{\text{  }}{\text{C}}}-\text{OH}$ | 2.8                    |
| Glutamic Acid | Glu(E)        | $\text{O}=\overset{\text{OH}}{\underset{\text{  }}{\text{C}}}-\text{CH}_2-\text{CH}_2-\underset{\text{C}=\text{O}}{\overset{\text{NH}_2}{\text{CH}}}-\text{OH}$           | 3.2                    |

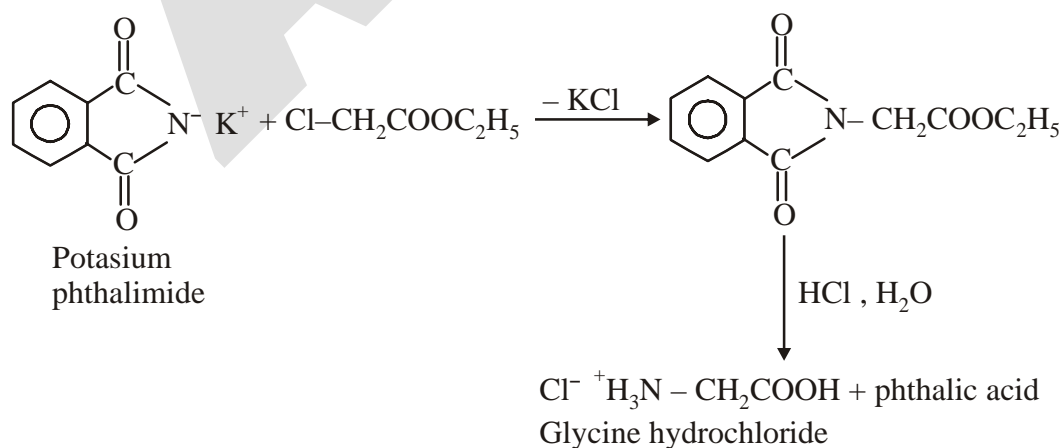
| <i>C - Basic amino acids (side chain with nitrogenous basic group)</i> |               |                                                                                                                                                                                                                                     |                       |
|------------------------------------------------------------------------|---------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| NAME                                                                   | ABBREVIATIONS | STRUCTURAL FORMULAE                                                                                                                                                                                                                 | ISOELECTRIC POINT[pI] |
| Lystine*                                                               | Lys(K)        | $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH} \begin{array}{l} \nearrow \text{NH}_2 \\ \searrow \text{C}=\text{O} \\ \quad \text{OH} \end{array}$                                                   | 9.7                   |
| Arginine*                                                              | Arg(R)        | $\text{H}_2\text{N}-\overset{\text{NH}}{\underset{\text{  }}{\text{C}}}-\text{NH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH} \begin{array}{l} \nearrow \text{NH}_2 \\ \searrow \text{C}=\text{O} \\ \quad \text{OH} \end{array}$ | 10.8                  |
| Histidine*                                                             | His(H)        |                                                                                                                                                   | 7.6                   |

**Note:**

- \* Amino acids with an asterisk are essential amino acids.
- † At pH = 7, Asp and Glu have a net negative charge and exist as anions. At pH = 7, Lys and Arg have a net positive charge and exist as cations. Rest of the amino acids at this pH exist in the neutral form.
- ‡ Structurally, in cystine, the two cysteine molecules are joined through sulfur (disulfide linkage).
- @@ Proline is an  $\alpha$ -imino acid, all amino acids are primary amines except proline and 4-hydroxyproline, which are 2° amines.
- @ Except Glycine all other amino acids are optically active.

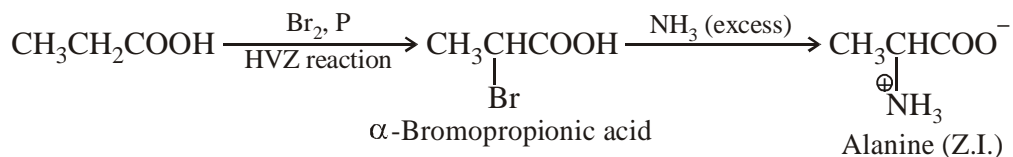
**Preparation of amino acids****(a) Gabriel Phthalimide synthesis**

Good yields of amino acids are generally obtained by the Gabriel phthalimide synthesis ; In this method  $\alpha$  - halo esters are used instead of  $\alpha$  - halo acids .

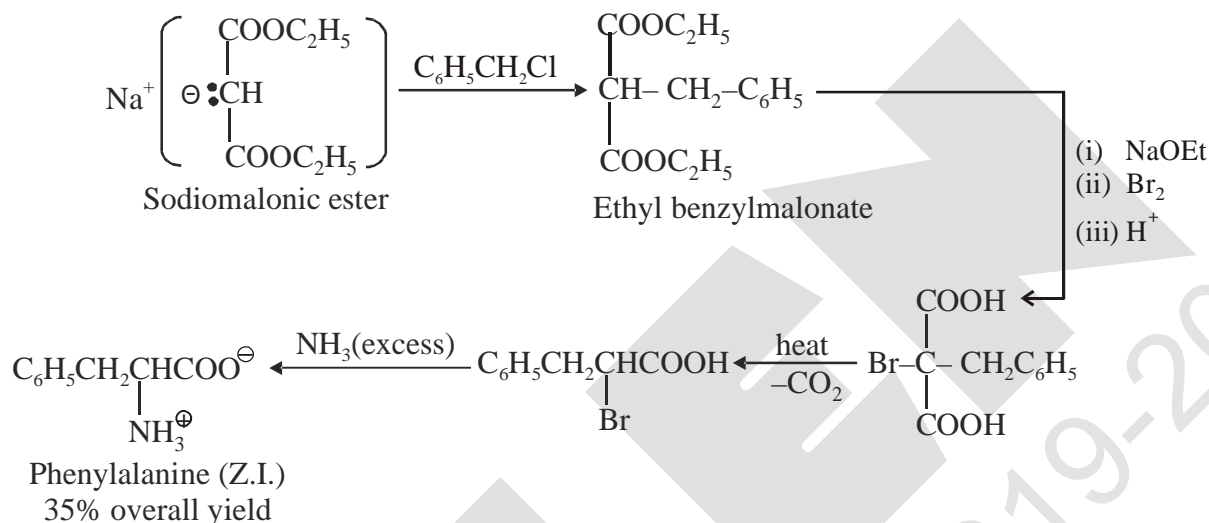


(b) **Amination of  $\alpha$  - Halo acids**

Sometimes an  $\alpha$  - chloro or  $\alpha$  - bromo acid is subjected to direct ammonolysis with excess of concentrated ammonia.

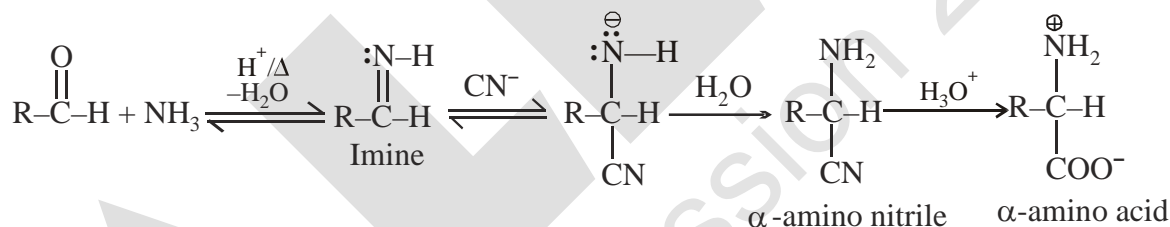


(c) **From diethyl malonate**

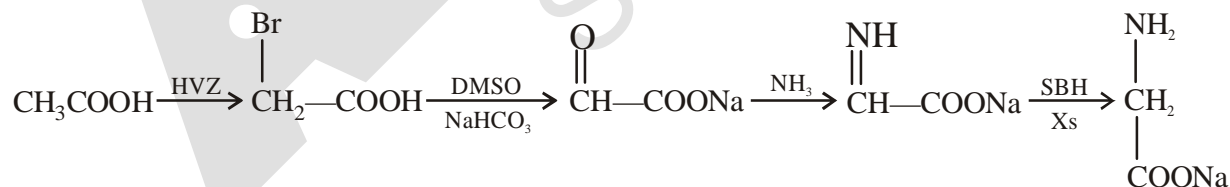


(d) **Strecker's synthesis**

Strecker's synthesis is also used for preparing  $\alpha$  - amino acids



(e) **Using KOOP synthesis**



**Properties of Amino acids**

Although the amino acids are commonly shown as containing an amino group and a carboxyl group,  $\text{H}_2\text{NCH(R)COOH}$ , certain properties, (both physical and chemical) are not consistent with this structure

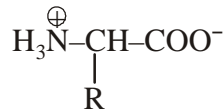
**I. Physical properties**

In contrast to amines and carboxylic acids, the amino acids are nonvolatile crystalline solids, which melt with decomposition at fairly high temperatures. They are insoluble in non-polar solvents like petroleum ether, benzene or ether and are appreciably soluble in water. Their aqueous solutions behave like solutions of substances of high dipole moment due to existence.

**Amino acids as dipolar ions as zwitter ion**

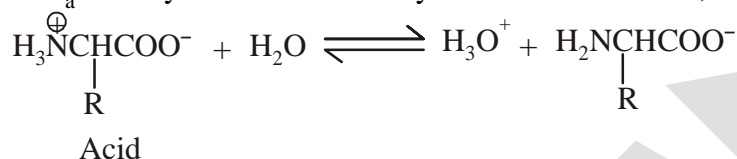
Acidity and basicity constant are ridiculously low for  $-\text{COOH}$  and  $-\text{NH}_2$  groups. Glycine, for example, has  $K_a = 1.6 \times 10^{-10}$  and  $K_b = 2.5 \times 10^{-12}$ , whereas most carboxylic acids have  $K_a$  values of about  $10^{-5}$  and most aliphatic amines have  $K_b$  values of about  $10^{-4}$ .

All these properties are quite consistent with a dipolar ion structure for the amino acids (I)



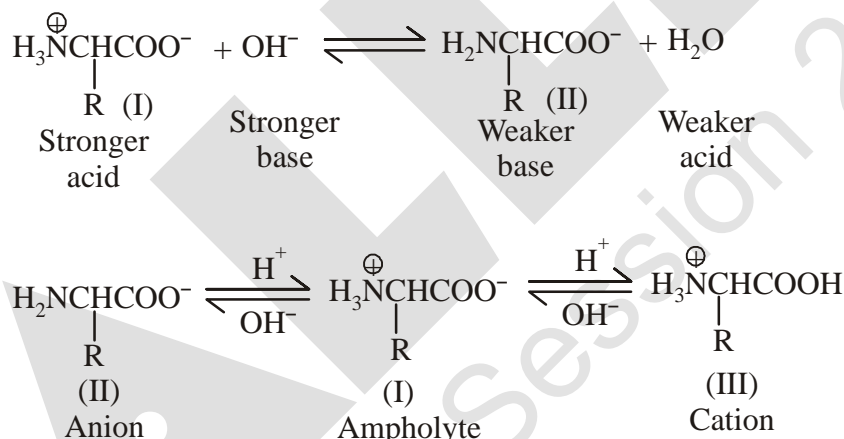
Amino acids : dipolar ions (Zwitter ion)

Physical properties - melting point, solubility, high dipole moment - are just what would be expected of such a salt. The acid-base properties also become understandable when it is realized that the measured  $K_a$  actually refers to the acidity of an ammonium ion,  $\text{RNH}_3^+$ ,



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{H}_2\text{NCHRCOO}^-]}{[\text{H}_3\text{NCHRCOO}^+]}$$

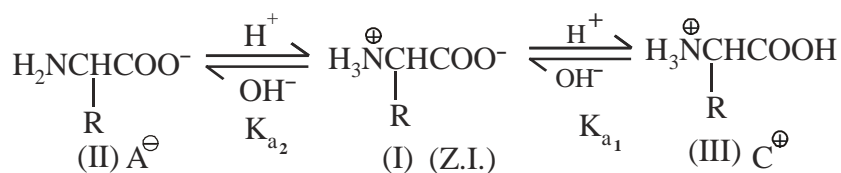
When the solution of an amino acid is made alkaline, the dipolar ion (I) is converted into the anion (II). The stronger base, hydroxide ion, removes a proton from the ammonium ion and displaces the weaker base, the amine.



Wherever feasible, we can speed up a desired reaction by adjusting the acidity or basicity of the solution in such a way as to increase the concentration of the reactive species.

**Isoelectric point of amino acids**

What happens when a solution of an amino acid is placed in an electric field depends upon the of the solution.



In quite alkaline solution, anions (II) exceed cations (III), and there is a net migration of amino acid toward the anode. In quite acidic solution, cations (III) are in excess, and there is a net migration of amino acid toward the cathode. If (II) and (III) are exactly balanced, there is no net migration; under such conditions any one molecule exists as a positive ion and as a negative ion for exactly the same amount of time, and any small movement in the direction of one electrode is subsequently cancelled by an equal movement back towards the other electrode. **The hydrogen ion concentration of the solution in which a particular amino acid does not migrate under the influence of an electric field is called the isoelectric point (pI) of that amino acid. The isoelectric point (pI) is the pH at which the amino acid exists only as a dipolar ion with net charge zero.**

For glycine, for example, the isoelectric point is at pH 6.1.

An amino acid usually shows its lower solubility in a solution at the isoelectric point, since here there is the highest concentration of the dipolar ion. As the solution is made more alkaline or more acidic, the concentration of one of the more soluble ions, (II) or (III) increases.

$$K_{a1} = \frac{[Z.L.][H^+]}{[C^+]}, \quad K_{a2} = \frac{[A^-][H^+]}{[DI]} \quad \text{at pI } [A^\ominus] = [C^\oplus]$$

$$\frac{[Z.L.][H^+]}{K_{a1}} = \frac{K_{a2}[DI]}{[H^+]} \quad [H^+]^2 = K_{a1} \& K_{a2}$$

$$\text{on taking antilog pI} = \frac{pK_{a1} + pK_{a2}}{2}$$

An amino acid having  $-\text{COOH}$  group more than  $\text{NH}_2$  group or such amino acid have pI less than 7.

An amino acid having more  $-\text{NH}_2$  more than  $\text{COOH}$  group such amino acid have pI more than 7.

Q. Write the structure of alanine at pH 2.5, 10.5 and 6.

### Electrophoresis

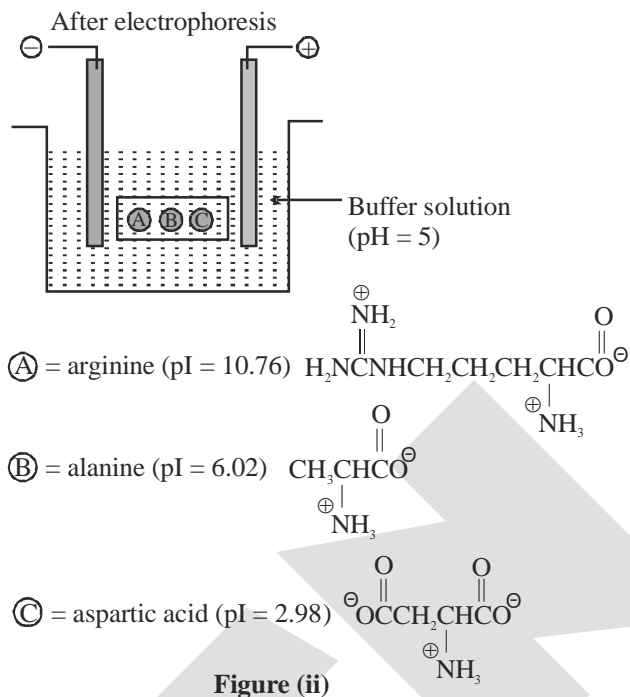
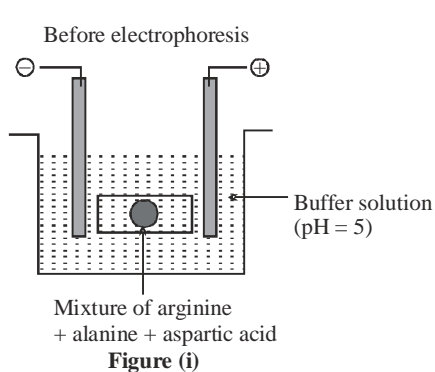
The movement of charged molecules (like amino acid) under the influence of an electric field is called electrophoresis. Electrophoresis separates amino acids on the basis of their pI values.

Amino acid is positively charged (moves towards cathode) if pH of the solution  $<$  pI

Amino acid is negatively charged (moves towards anode) if pH of the solution  $>$  pI

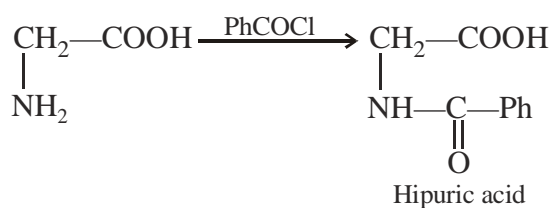
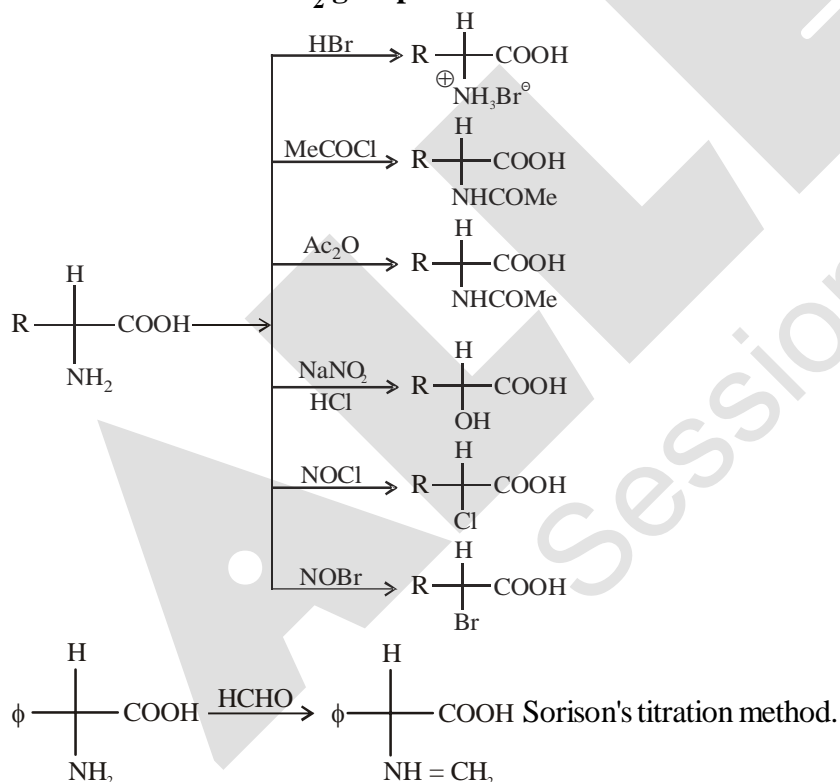
Q. How will you separate a ternary mixture of arginine, alanine & aspartic acid?

**Ans.** A few drops of a solution of an amino acid mixture are applied to the middle of a piece of filter paper. When the paper is placed in a buffer solution (pH = 5) between the two electrodes and an electric field is applied then arginine & alanine with  $pI > pH$  move towards the cathode and aspartic acid with  $pI < pH$  moves towards the anode. Out of arginine & alanine, alanine will move slowly towards the cathode due to lesser positive charge.



## General reactions of amino acids

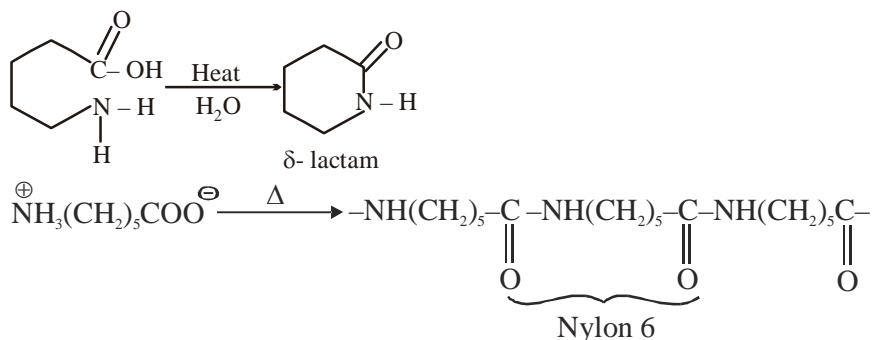
(1) **Reactions due to  $-\text{NH}_2$  group**



Reactions is used to block  $-NH_2$  group during volumetric analysis in.





(4) **Peptide**

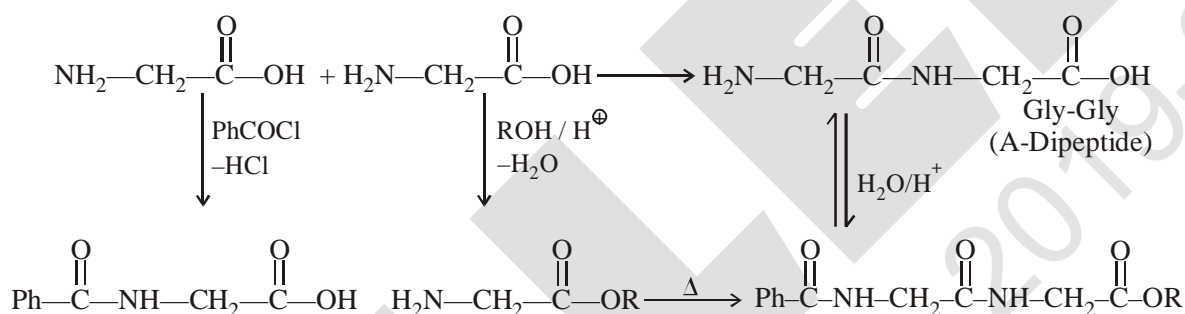
A peptide is a kind of amide formed by intermolecular reaction of the amino group of one amino acid and the carboxyl group of a second amino acid. Dipeptides are made from two amino acids, tripeptides from three amino acids, etc, which may be the same or different. If there are three to ten amino acid residues, the peptide is also called an oligopeptide.

If they give 3 to 10 amino acid they are oligopeptide

If they give 11 to 100 amino acid they are Polypeptide

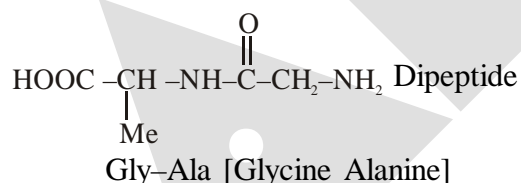
For more than 100 it is Macropeptide

- Peptides can be prepared by blocking technique

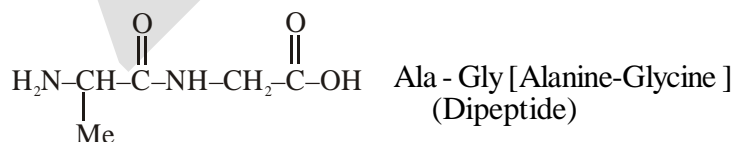


Firstly, the amino and carboxyl groups that are not to be linked in peptide bonds must be blocked to make unreactive.

Abbreviated name of amino acid with free  $\text{NH}_2$  is written first.



By convention, the amino acid with the free amino group (N-terminal) is written at the left end and the one with the unreacted carboxyl group (C-terminal) at the right end.



- When different amino acids are involved in peptide formation.

Then total number of polypeptide possible =  $X^n$

[X = type of amino acid interacting,

n = number of amino acid molecule are interacting.]

- Q. Glycine can form how many Dipeptide ? [Ans. One]  
 Q. Glycine can form how many Tripeptide ? [Ans. One]  
 Q. Glycine and Ala can form how many Dipeptide ? [Ans. Four]  
 Q. Gly, Ala, and Phenyl Ala can form how many Dipeptide ? [Ans. Nine]  
 Q. Gly, Ala, can form how many Tripeptide ? [Ans. Eight]

A polypeptide with more than hundred amino acid residues, having molecular mass higher than 10,000 is called a protein. However, the distinction between a polypeptide and a protein is not very sharp. Polypeptides with fewer amino acids are likely to be called proteins they ordinarily have a well defined conformation of a protein such as insulin which contains 51 amino acids.

Proteins can be classified into two types on the basis of their molecular shape.

(a) **Fibrous proteins**

When the polypeptide chains run parallel and are held together by hydrogen and disulphide bonds, then fibre-like structure is formed. Such proteins are generally insoluble in water. Some common examples are keratin (present in hair, wool, silk) and myosin (present in muscles), etc.

(b) **Globular proteins**

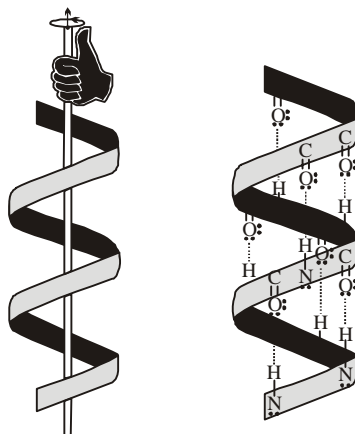
This structure results when the chains of polypeptides coil around to give a spherical shape. These are usually soluble in water. Insulin and albumins are the common examples of globular proteins.

**Structure of Proteins**

Structure and shape of proteins can be studied at four different levels, i.e., primary, secondary, tertiary and quaternary, each level being more complex than the previous one.

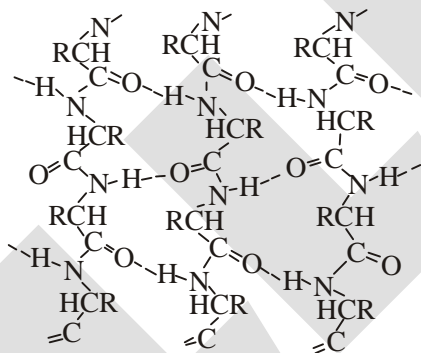
- (i) **Primary structure of proteins :** Proteins may have one or more polypeptide chains. Each polypeptide in a protein has amino acids linked with each other in a specific sequence and it is this sequence of amino acids that is said to be the primary structure of the protein. Any change in this primary structure i.e., the sequence of amino acids creates a different protein.
- (ii) **Secondary structure of proteins :** The secondary structure of protein refers to the shape in which a long polypeptide chain can exist. They are found to exist in two different types of structures viz.  $\alpha$ -helix and  $\beta$ -pleated sheet structure. These structures arise due to the regular folding of the backbone

of the polypeptide chain due to hydrogen bonding between  $\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—}$  and  $\text{—NH—}$  groups of the peptide bond.

 $\alpha$ -Helix structure of proteins

$\alpha$ -Helix is one of the most common ways in which a polypeptide chain forms all possible hydrogen bonds by twisting into a right handed screw (helix) with the —NH group of each amino acid residue hydrogen bonded to the  $\text{C}=\text{O}$  of an adjacent turn of the helix as shown in figure.

In  $\beta$ -structure all peptide chains are stretched out to nearly maximum extension and then laid side by side which are held together, by intermolecular hydrogen bonds. The structure resembles the pleated folds of drapery and therefore is known as  $\beta$ -pleated sheet.

 $\beta$ -Pleated sheet structure of proteins

- (i) Ionic bonding : between  $\text{COO}^-$  and  $\text{NH}_3^+$  at different sites.
- (ii) H-bonding : mainly between side-chain  $\text{NH}_2$  and  $\text{COOH}$ , also involving OH's (Of serine, for example) and the N—H of tryptophan.
- (iii) Weakly hydrophobic Van der Waal's attractive forces engendered by side-chain R groups and
- (iv) Disulfide cross linkages between loops of the polypeptide chain.

The same kind of attractive and repulsive forces responsible for the tertiary structure operate to hold together and stabilize the subunits of the quaternary structure.

- (iii) **Tertiary structure of proteins :** The tertiary structure of proteins represents overall folding of the polypeptide chains i.e., further folding of the secondary structure. It gives rise to two major molecular shapes viz. fibrous and globular. The main forces which stabilise the  $2^\circ$  and  $3^\circ$  structures of proteins are hydrogen bonds, disulphide linkages, van der Waals and electrostatic forces of attraction.

- (iv) **Quaternary structure of proteins :** Some of the proteins are composed of two or more polypeptide chains referred to as sub-units. The spatial arrangement of these subunits with respect to each other is known as quaternary structure. Example : Hemoglobin, Chlorophyll.

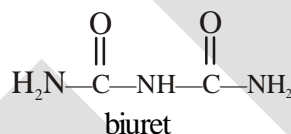
According to their biological action, they are classified as enzymes, hormones, antibodies, etc.

Protein found in living system with definite configuration and biological activity is termed as native protein. If a native protein is subjected to physical or chemical treatment, which may disrupt its higher structures (conformations) without affecting its primary structure, the protein is said to be denatured. During denaturation, the protein molecule uncoils from an ordered and specific conformation into a more random conformation leading to precipitation. Thus denaturation leads to increase in entropy and loss of biological activity of the protein. The denaturation may be reversible or irreversible. Thus, the coagulation of egg white on boiling of egg protein is an example of irreversible protein denaturation. However, in certain cases it is found that if the disruptive agent is removed the protein recovers its original physical and chemical properties and biological activity the reverse of denaturation is known as renaturation.

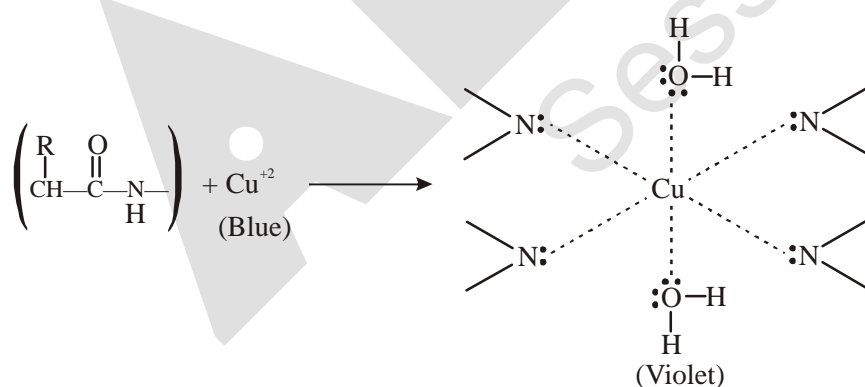
### Tests of Proteins:

**Biuret test :** Addition of a very dilute solution of  $\text{CuSO}_4$  to an alkaline solution of a protein is done. A positive test is indicated by the formation of a pink violet to purple violet color.

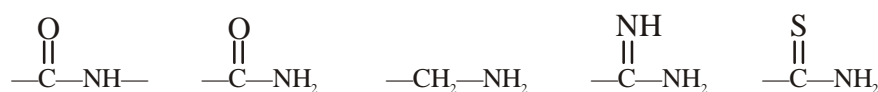
The name of test is derived from a specific compound, biuret, which gives a positive test with this reagent



When a protein reacts with copper (II) sulfate (blue), the positive test is the formation of a violet colored complex.

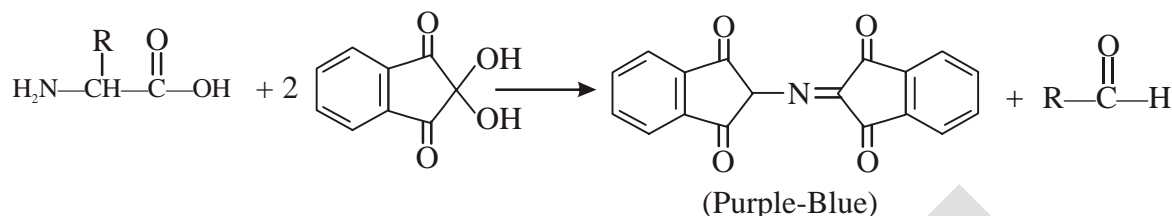


The biuret test works for any compound containing two or more of the following groups.



**Ninhydrin Test :** The ninhydrin test is a test for amino acids and proteins with a free  $-\text{NH}_2$  group.

Amino acids are detected by ninhydrin test. All amino acids give violet - coloured product with ninhydrin (triketo hydroindene hydrate) except proline and 4 - hydroxy proline, which gives yellow colour with it. When such an  $\text{-NH}_2$  group reacts with ninhydrin, a purple-blue complex is formed.



The same violet coloured dye forms from all  $\alpha$  - AA's with  $1^\circ$  amino groups because only their nitrogen is incorporated into it. The  $2^\circ$  amines proline and 4 - hydroxyproline give different adducts that absorb light at a different and thus have a different yellow colour.

## CARBOHYDRATES

Carbohydrates (hydrates of carbon) are naturally occurring compounds having general formula  $\text{C}_x(\text{H}_2\text{O})_y$ , which are constantly produced in nature & participate in many important bio-chemical reactions.

|                      |                                         |                                        |
|----------------------|-----------------------------------------|----------------------------------------|
| Ex. - Glucose        | $\text{C}_6\text{H}_{12}\text{O}_6$     | $\text{C}_6(\text{H}_2\text{O})_6$     |
| Fructose             | $\text{C}_6\text{H}_{12}\text{O}_6$     | $\text{C}_6(\text{H}_2\text{O})_6$     |
| Cellulose and Starch | $(\text{C}_6\text{H}_{10}\text{O}_5)_n$ | $(\text{C}_6(\text{H}_2\text{O})_5)_n$ |

- Sucrose (Cane sugar) -  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , and
- Maltose (Malt Sugar)  $\text{C}_{12}(\text{H}_2\text{O})_{11}$

But some compounds which have formula according to  $\text{C}_x(\text{H}_2\text{O})_y$  are not known as carbohydrate

|     |                                    |              |
|-----|------------------------------------|--------------|
| Ex. | $\text{CH}_2\text{O}$              | Formaldehyde |
|     | $\text{C}_2(\text{H}_2\text{O})_2$ | Acetic acid  |
|     | $\text{C}_3(\text{H}_2\text{O})_3$ | Lactic acid  |

There are many compounds, which show chemical behaviour of carbohydrate but do not confirm the general formula  $\text{C}_x(\text{H}_2\text{O})_y$  such as -  $\text{C}_5\text{H}_{10}\text{O}_4$  (2-deoxyribose),  $\text{C}_6\text{H}_{12}\text{O}_5$  (Rahmnose)  
 $\text{C}_7\text{H}_{14}\text{O}_6$  (Rahmnohexose)

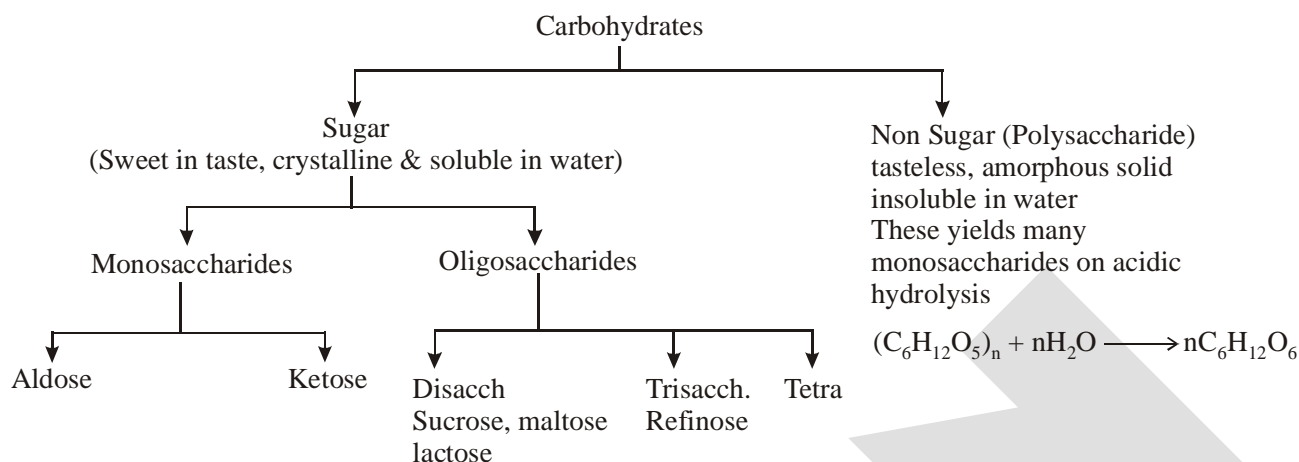
**Modern Concept :** Carbohydrates are polyhydroxy aldehyde or ketone

or

Substances which yield these (polyhydroxy aldehyde or ketone) on hydrolysis

- Carbohydrates  $\xrightarrow{\text{H}_2\text{O}/\text{H}^+}$  Polyhydroxy aldehyde or ketone
- Carbohydrates are also known as Saccharides.
- In plants carbohydrates are synthesised by photosynthesis

### Classification of carbohydrates :



### Monosaccharides : (simple sugars)

These are the sugars which cannot be hydrolysed into smaller molecules.

General formula is  $C_nH_{2n}O_n$

Ex. - Glucose, Fructose, Ribose, Deoxyribose

- If aldehyde group is present in monosaccharide, then it is known as aldose.
- If ketone group is present in monosaccharide, then it is known as ketose.

### Oligosaccharides :-

These are the sugars which yields 2–10 monosaccharides units on hydrolysis. such as.

These are of following types

(a) *Disaccharides* :- Gives two monosaccharide unit on hydrolysis (may or may not be same).

Ex. - Sucrose, Maltose, Lactose

(b) *Trisaccharides* :- Gives Three monosaccharide unit on hydrolysis.

Polysaccharides :- These are the non sugars which yield a large no of monosaccharide units on hydrolysis

General formula -  $(C_6H_{10}O_5)_n$ . Ex.- Starch, Cellulose, Glycogen

**Note** :- A group of polysaccharides which are not so widely used in nature is pentosans  $(C_5H_8O_4)_n$

Monosaccharides, General formula  $C_x(H_2O)_y$   $x = 3 - 8$ . Nomenclature of monosaccharides are given according to the no. of carbons present in them.

On the basis of C-atom monosaccharides can be farther classified as, Trioses, Tetras, Pentoses, Hexoses.

Table

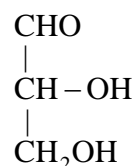
|    |                                   | Aldoses               | Ketoses                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |
|----|-----------------------------------|-----------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 3C | Triose or Triose                  | Aldotriose            | Ketotriose                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |
| 4C | Tetrose                           | Aldotetrose           | Ketotetrose                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |
| 5C | Pentose                           | Aldopentose           | Ketopentose                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |
| 5C | Including $-\text{CHO}$           | Aldopentose (Ribose)  | $  \begin{array}{c}  \text{H}-\text{C}=\text{O} \\    \\  \text{H}-\text{C}-\text{OH} \\    \\  \text{H}-\text{C}-\text{OH} \\    \\  \text{H}-\text{C}-\text{OH} \\    \\  \text{CH}_2\text{OH}  \end{array}  $                                                                                                                                                                                                                                                                                                 |
| 5C | Including $-\text{C}(=\text{O})-$ | Ketopentose           | $  \begin{array}{c}  \text{CH}_2\text{OH} \\    \\  \text{C}=\text{O} \\    \\  \text{H}-\text{C}-\text{OH} \\    \\  \text{H}-\text{C}-\text{OH} \\    \\  \text{CH}_2\text{OH}  \end{array}  \text{ (Ributose)}  $                                                                                                                                                                                                                                                                                             |
| 6C | Hexose                            | Aldohexose            | Ketohexose                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |
| 6C | Including $-\text{CHO}$           | Aldohexose (Glucose)  | $  \begin{array}{c}  \text{CHO} \\    \\  \text{H}-\text{C}-\text{OH} \\    \\  \text{HO}-\text{C}-\text{H} \\    \\  \text{H}-\text{C}-\text{OH} \\    \\  \text{H}-\text{C}-\text{OH} \\    \\  \text{CH}_2\text{OH}  \end{array}  $ <p>D-glucose</p> $  \begin{array}{c}  \text{CH}_2\text{OH} \\    \\  \text{C}=\text{O} \\    \\  \text{HO}-\text{C}-\text{H} \\    \\  \text{H}-\text{C}-\text{OH} \\    \\  \text{H}-\text{C}-\text{OH} \\    \\  \text{CH}_2\text{OH}  \end{array}  $ <p>D-fructose</p> |
| 6C | Including $-\text{C}(=\text{O})-$ | Ketohexose (Fructose) |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |

## Stereochemistry of carbohydrates :

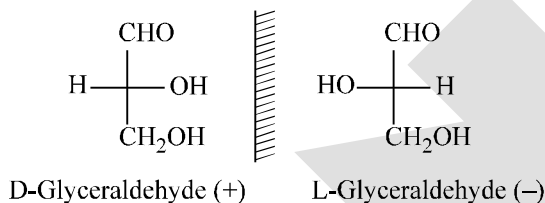
**D & L-Sugars :** The series of aldoses or ketoses in which the configuration of the penultimate C-atom (C-next to  $\text{CH}_2\text{-OH}$  group) is described as D-sugars if  $\text{-OH}$  is towards RHS & L-sugars if it is towards LHS.

Smallest carbohydrate

- \* Aldotriose
- \* Glyceraldehyde

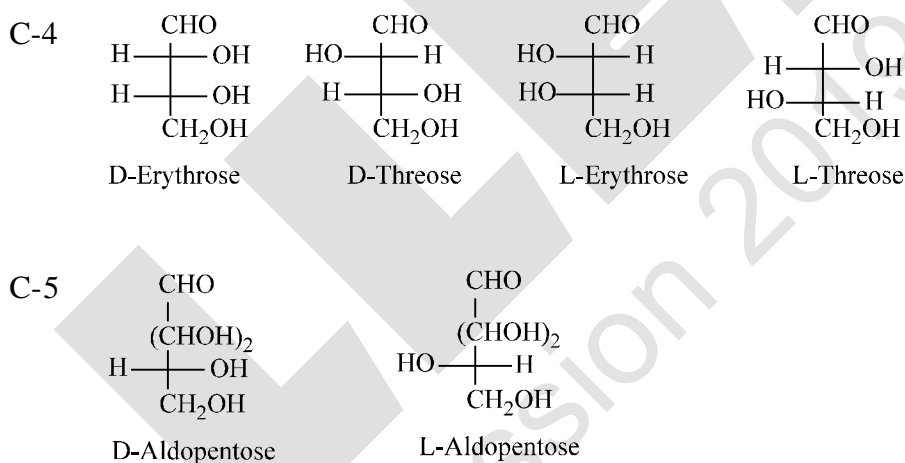


Fischer projection



### Classification of Aldotetros :

- (i) Erythrose
- (ii) Threose



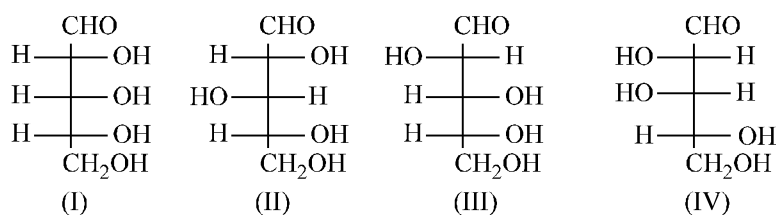
No. of  $\text{C}^* = 3$  (in Aldopentose)

No. of optical isomers  $2^3 = 8$

No. of D Sugars 4

No. of L Sugars 4

### D-Aldopentose :



All Isomeric D-sugars are diastereomers.



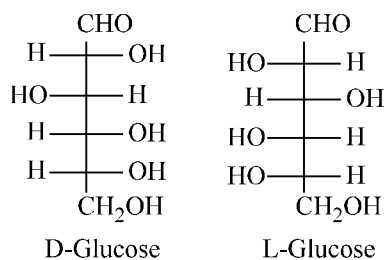
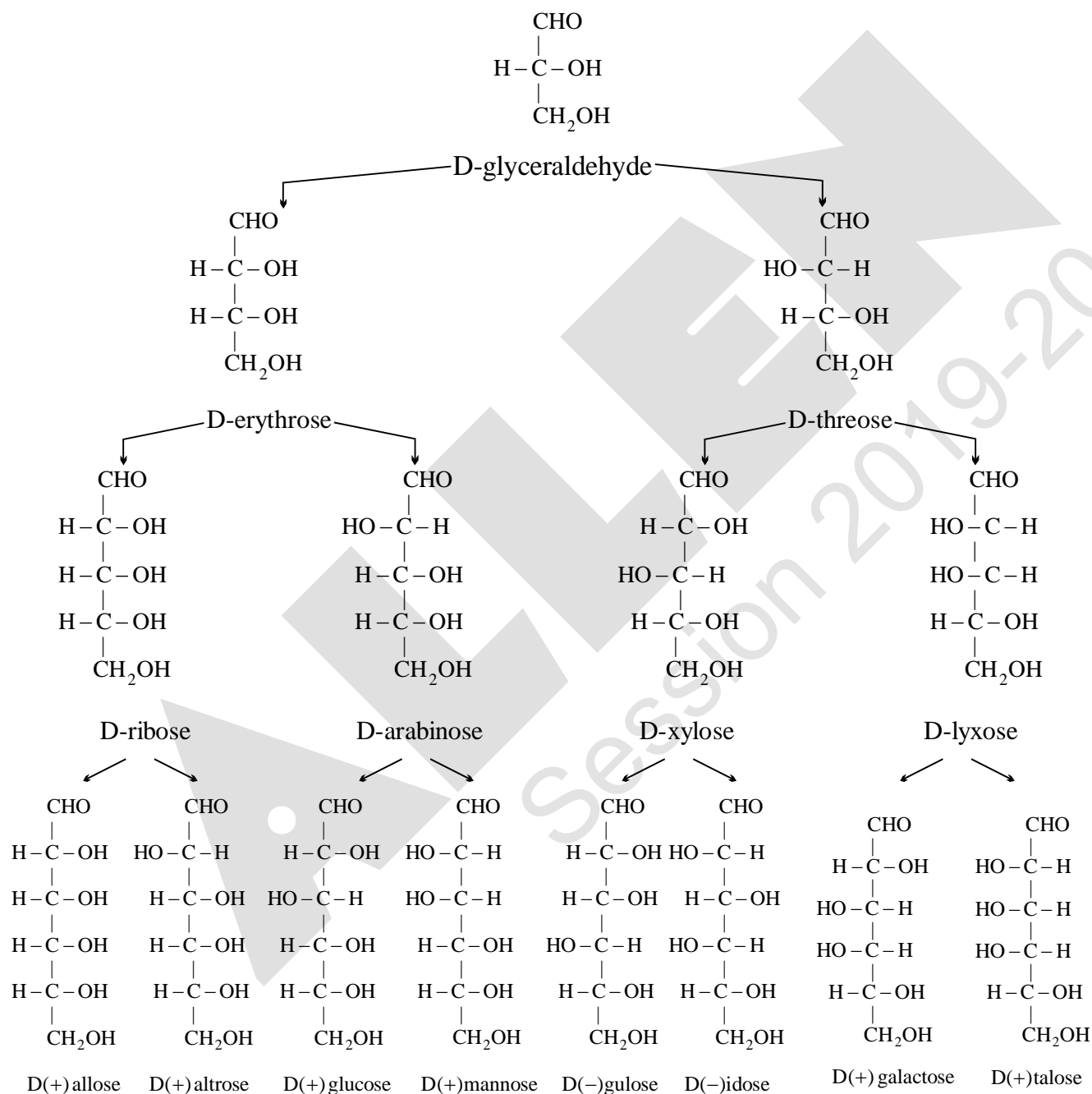
**Aldohexose :**

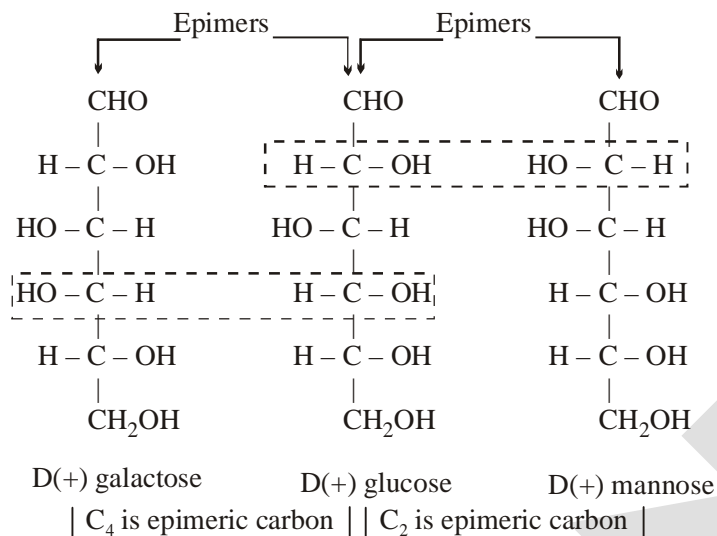
No. of C\* = 4

No. of stereoisomers =  $2^4 = 16$ 

No. of D-sugars = 8

No. of L-sugars = 8

**The D-family aldoses**



Another example with C<sub>2</sub> epimeric carbon is

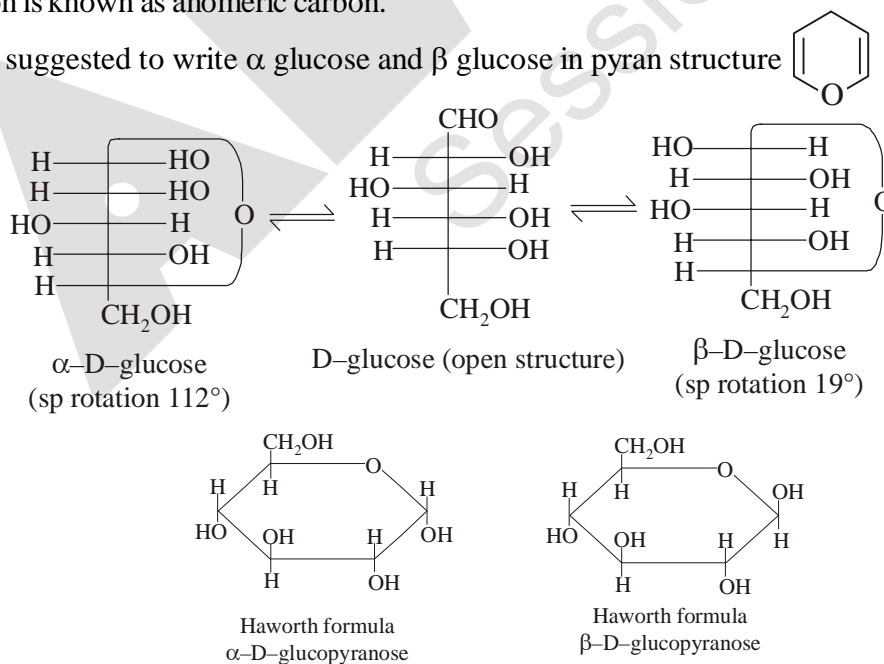


**Anomers:** Anomers are the stereoisomers which differs at a single chiral centre out of many & are ring chain tautomer of the same open chain compound.

The two sugars that differs in configuration only on the carbon that was the carbonyl carbon in the open chain form is called as anomers  $\alpha$  glucose and  $\beta$  glucose are known as anomers their equilibrium mixture contains 36 %  $\alpha$ -D-glucose , 63.8 %  $\beta$ -D-glucose and 0.2 % open chain form.

C<sub>1</sub> Carbon is known as anomeric carbon.

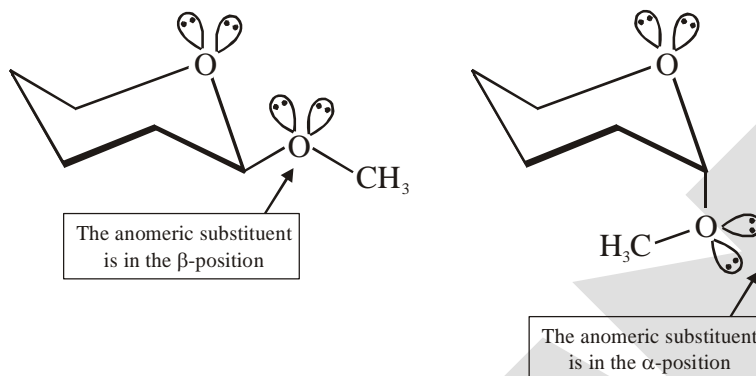
Haworth suggested to write  $\alpha$  glucose and  $\beta$  glucose in pyran structure



Anomers are epimers but epimers may not be anomers.

**Anomeric effect :**

$\beta$ -D-glucose is more stable than  $\alpha$ -D glucose because there is more room for a substituent in the equatorial position. However when glucose reacts with an alcohol to form a glucoside, the major product is the  $\alpha$ -glucoside. The preference for the axial position by certain substituents bonded to the anomeric carbon is called anomeric effect.



What is responsible for the anomeric effect ? One clue is that all the substituents that prefer the axial position have lone pair electrons on the atom bonded to the ring. The lone pair electrons of the anomeric substituent have repulsive interaction with the lone pair electron of the ring oxygen if the anomeric substituent is the  $\beta$ -position, but not if it is the  $\alpha$ -position.

Apparently attractive interaction of the hydrogen of the anomeric OH group of D-glucose with the lone pair electron of the ring oxygen decreases the importance of the anomeric effect making  $\beta$ -D glucose more stable than  $\alpha$ -D glucose. However, when the hydrogen is replaced by an alkyl group, the anomeric effect decreases the stability of the  $\beta$ -position so,  $\alpha$ -glycosides are more stable than  $\beta$ -glycosides.

**Cyclic structures of monosaccharides**

Many five membered and six membered monosaccharides occur in cyclic form. Cyclic structures of monosaccharides are established by many experiments. The cyclic structure is due to intramolecular hemiacetal formation between aldo / keto group and OH of any one carbon. The ring formed are generally six membered (pyranose) or five membered (furanose). Each cyclization results in creation of a new asymmetric centre apart from the existing ones. The isomers resulting from cyclizations are called anomers. example, when D-glucose (open structure) cyclise, it gives  $\alpha$ -D-glucose and  $\beta$ -D-glucose.

**Haworth projection :-**

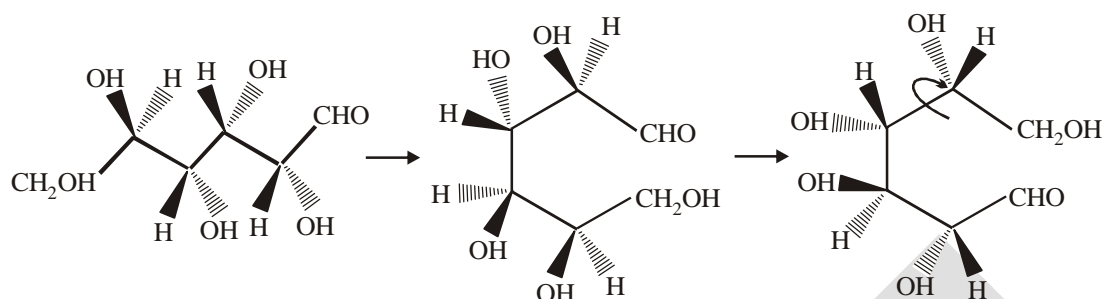
Many of monosaccharides form cyclic structures. The actual structure is almost planar and be represented by Haworth projection, which is a way of depicting three - dimensional cyclic structure.

**Rule -1 :-** In a Haworth projection draw a fisher projection in which ring oxygen is in a down position.

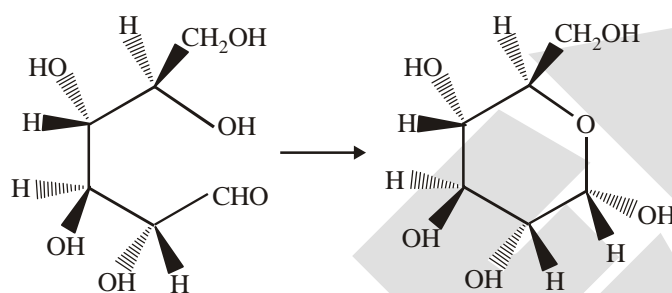
**Rule -2 :-** Imagine that carbon chain of fisher projection is folded around a barrel or drum, which provide a ring lies in a plane  $\perp$  to the page.

**Rule -3 :-** Now plane of ring is turned  $90^\circ$  so that anomeric carbon is on the right and the ring oxygen is in the rear. Obtained projection is a Haworth projection.

**Example :** (D-glucose)

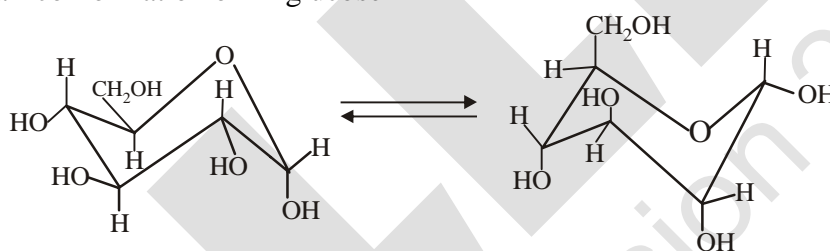


**Projection :**

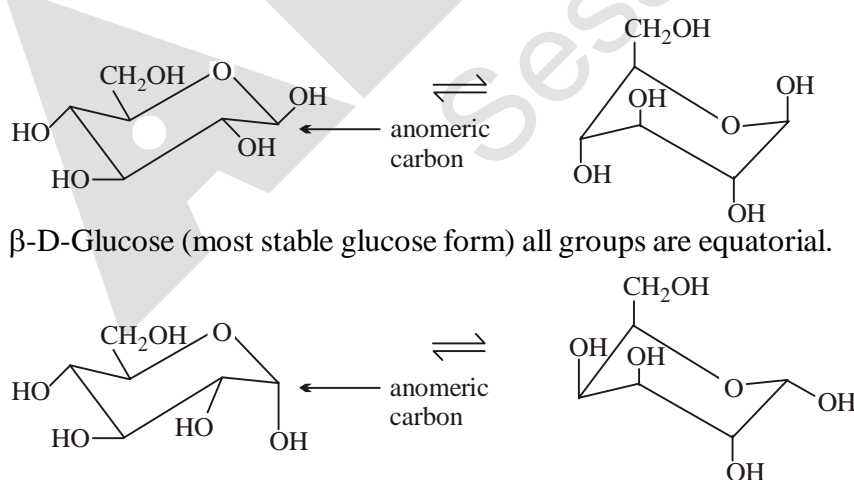


**Hawarth projection**

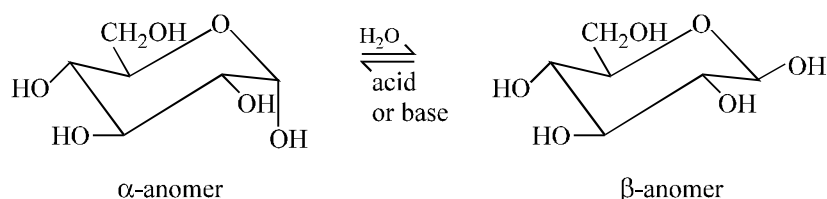
$\Rightarrow$  Chair conformation of D-glucose



**Chair forms of (conformation)  $\alpha$  and  $\beta$  D-Glucose :**



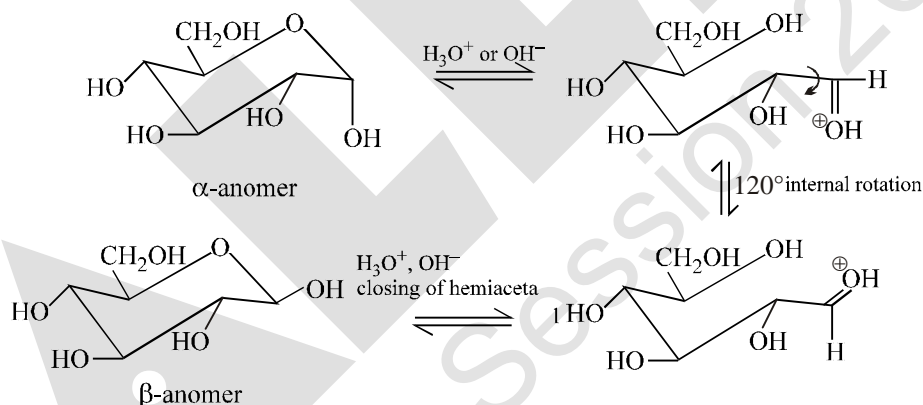
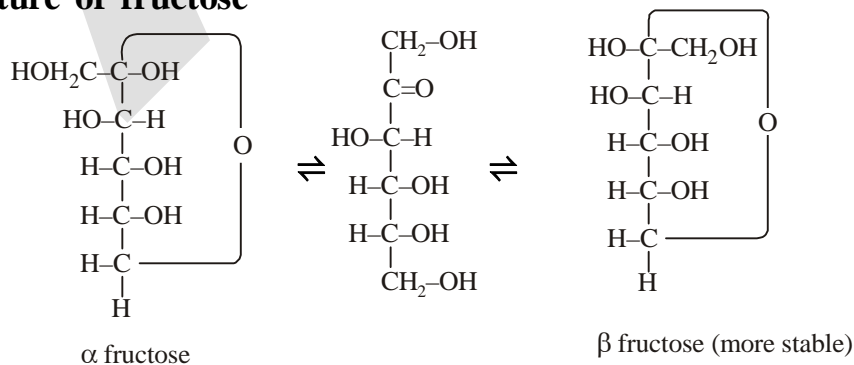
$\alpha$ -D-Glucose -OH group at anomeric carbon is axial.

**Mutarotation**Specific rotation of  $\alpha$  glucose  $+112^\circ$ Specific rotation of  $\beta$  glucose  $+19^\circ$ Equilibrium mixture  $[\alpha]_D = 52.5 \text{ degree mL g}^{-1} \text{ dm}^{-1}$ Fresh  $\alpha$ -glucose  $\longrightarrow 52.5 \longleftarrow$  Fresh  $\beta$ -glucose $112^\circ$ 36 %  $\alpha$  glucose $19^\circ$ 63.8 %  $\beta$  glucose

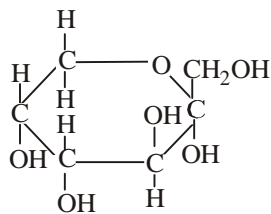
When pure  $\alpha$ -D glucose is dissolved in water its specific rotation is found to be  $+112^\circ$  with time, however the specific rotation of the solution decreases ultimately reaches stable value of  $+52.5^\circ$ . When  $\beta$ -D-glucose is dissolved in water, it has a specific rotation of  $19^\circ$ . The specific rotation of this solution increases with time also to  $+52.5^\circ$ .

This change of optical rotation with time is called mutarotation. It is caused by the conversion of  $\alpha$  and  $\beta$  glucopyranose anomers into an equilibrium mixture of both. Mutarotation is catalyzed by both acid and base, but also occurs even in pure water. Mutarotation is characteristic of the cyclic hemiacetal form of glucose.

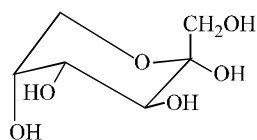
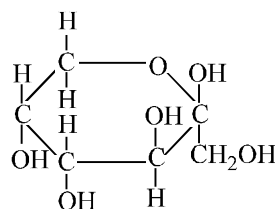
Mutarotation occurs first by opening of the pyranose ring to the free aldehyde form.

**Structure of fructose**

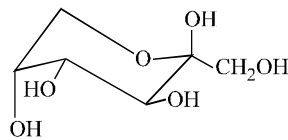
Ring structure of fructose C, Pyranose structures 6 membered ring,  $\text{C}_2 - \text{C}_6$  linkage



Chair conformations

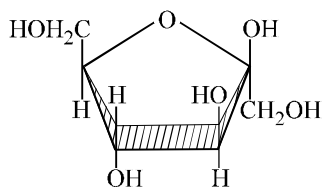


$\alpha$ -D-fructopyranose

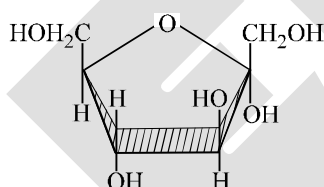


$\beta$ -D-fructopyranose

Furanose structure (5 membered ring)

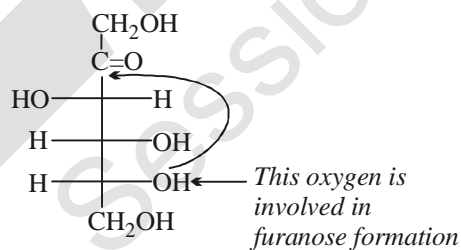
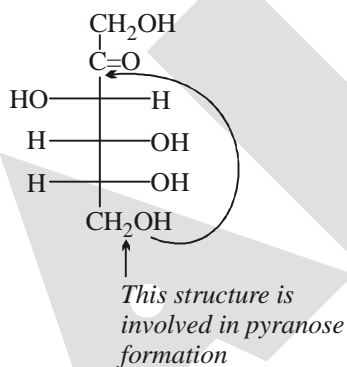


$\beta$ -D-fructofuranose

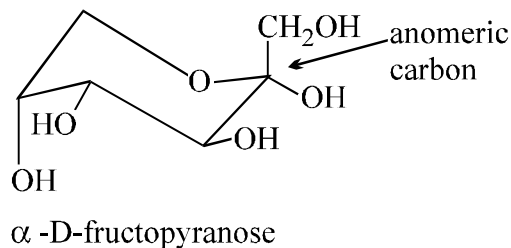
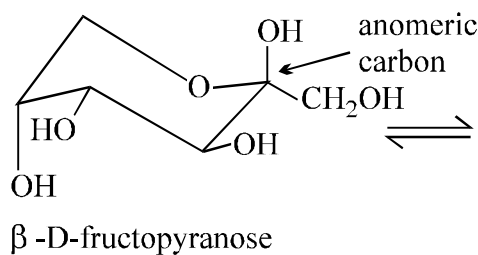


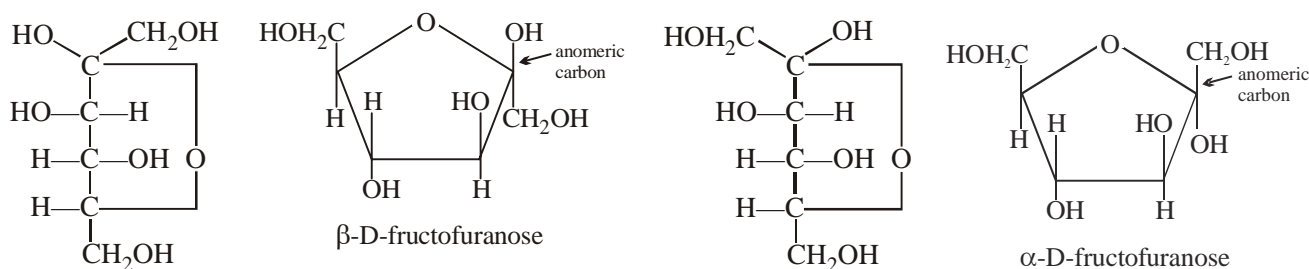
$\alpha$ -D-fructofuranose

**Mutarotation:** Fructose undergo complex mutarotation. The structure of the cyclic hemiacetal form of d-fructose can be derived from it's carbonyl (Ketone) form using the methods described as follows.



It happens that the crystalline form of D-fructose is  $\beta$ -D-Fructopyranose. When crystals of this form are dissolved in water, it equilibrates to both pyranose & furanose forms.

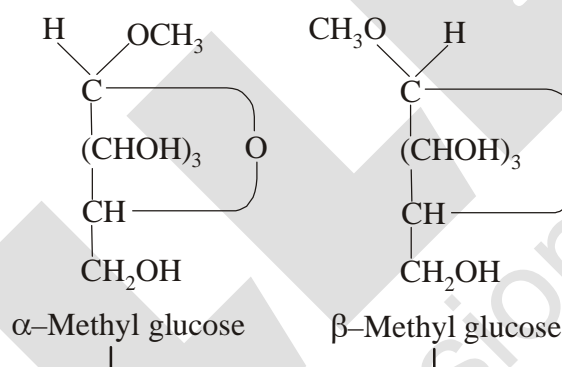




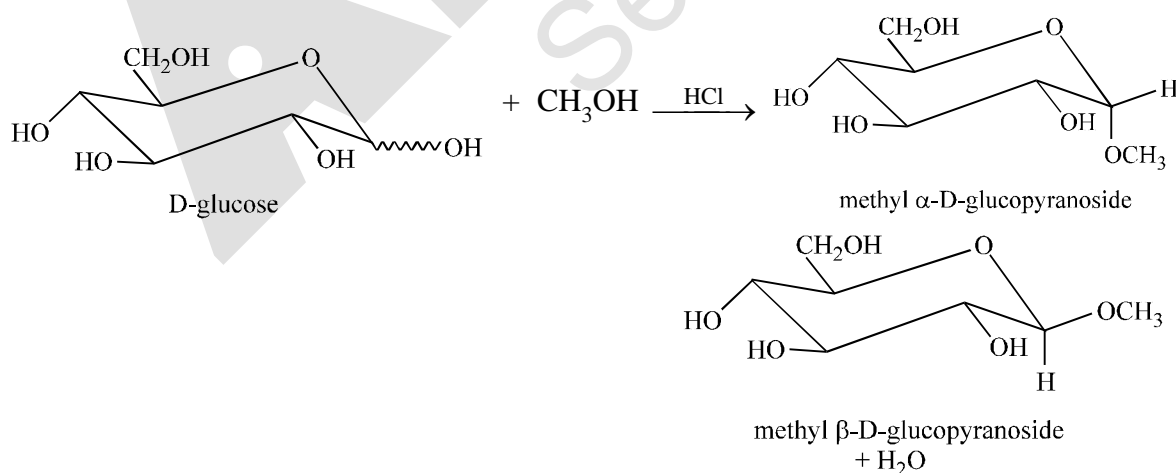
- \* All monosaccharides are reducing sugars and they show mutarotation.
- \* Starch, cellulose are Polymers of Glucose
- \* Lactose and sucrose are disaccharides
- \* Sucrose is a non reducing sugar, gives negative test for Benedict and tollen's reagent, they do not form osazone and do not show mutarotation.
- \* Acetals of carbohydrates are called as GLYCOSIDE

### Formation of Glycosides

Glucose reacts with methyl alcohol in presence of dry HCl to form  $\alpha$  and  $\beta$ -methyl glycoside of glucose. The reaction takes place only on OH of hemi-acetylic carbon. Other hydroxyl groups are unreactive.



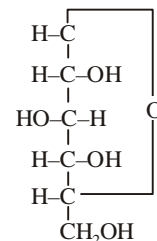
To methylate all the OH groups, methylating agent used is dimethyl sulphate.



Such compounds are called glucoside (cyclic acetals). They are special type of acetals in which one of the oxygen of the acetal linkage is the ring oxygen of the pyranose or furanose.

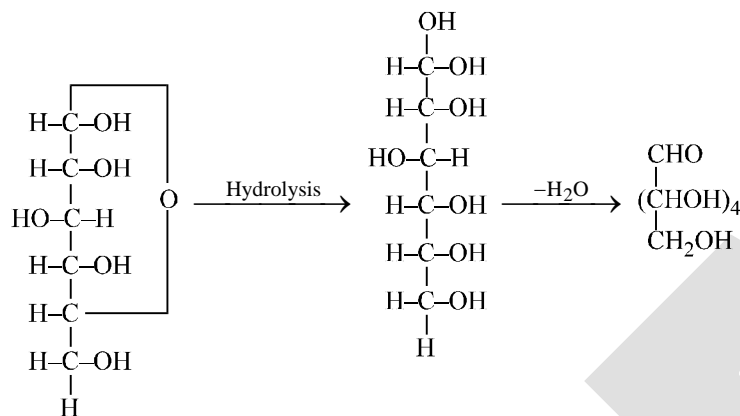
**Ring structure of glucose :**

- (i) Glucose does not give pink colour with schief reagent.
- (ii) Does not form adduct with  $\text{NaHSO}_3$ ,  $\text{NH}_3$
- (iii) Glucose exist in two isomeric form
- (iv) It show mutarotation

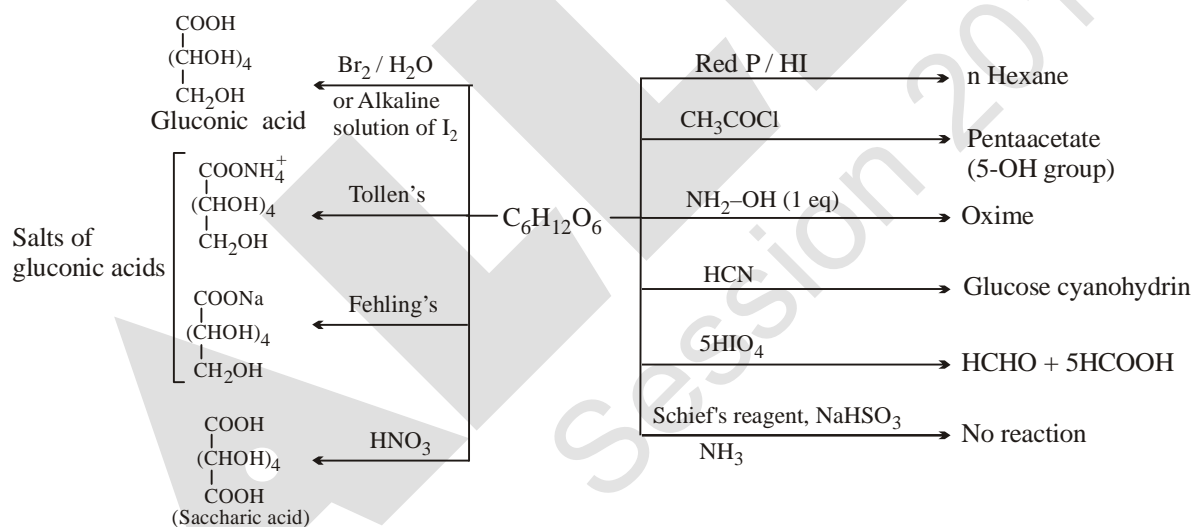


Since there is no free aldehyde group, so it does not react with weak reagent

( $\text{NH}_3$ ,  $\text{NaHSO}_3$ ) but strong reagent ( $\text{HCN}$ ,  $\text{NH}_2\text{OH}$ ,  $\text{C}_6\text{H}_5\text{NH}-\text{NH}_2$ ) break up ring

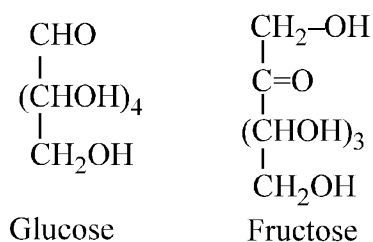


**REACTIONS OF GLUCOSE**



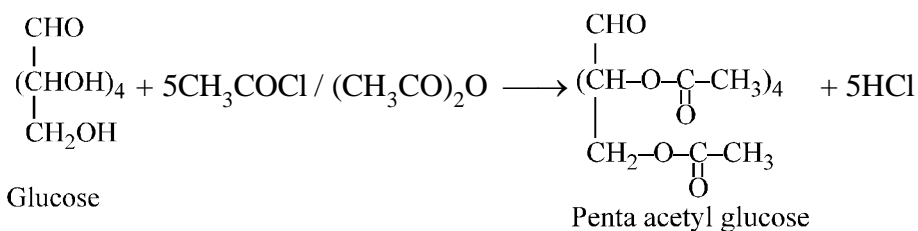
These reactions indicate that glucose has 6-C straight chain with one  $-\text{CHO}$  group & 5-OH group.

**General reactions of monosaccharies**



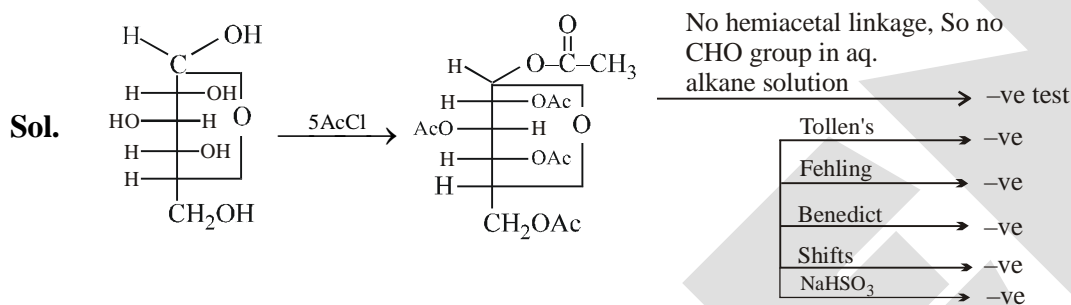


## 1. Acetylation :



This reaction suggests presence of 5(-OH) group.

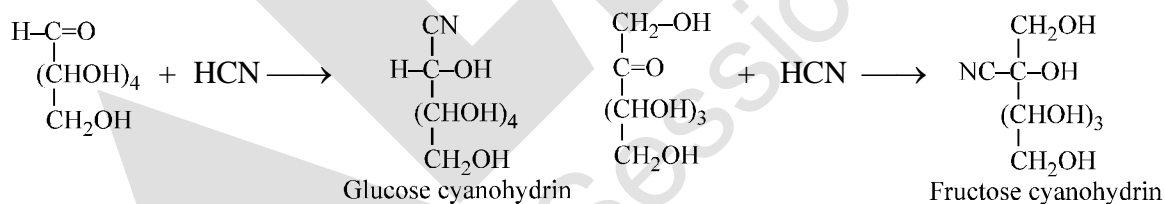
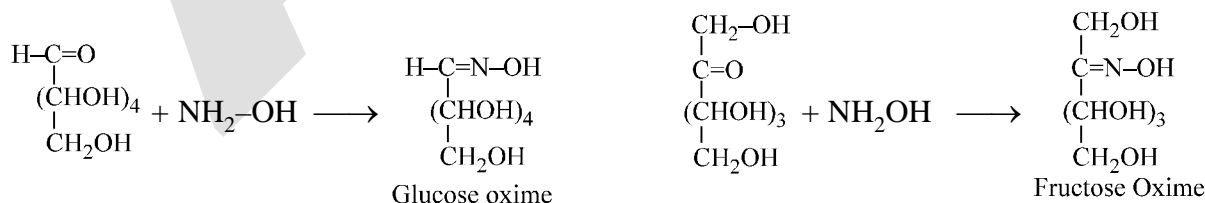
Q. The penta acetate of glucose give -ve test with Tollen's reagent & Fehling solution, explain?



## 2. Red by HI / Red P :

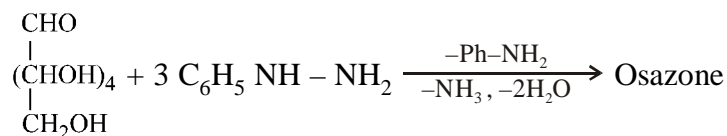


## 3. Reaction with HCN:

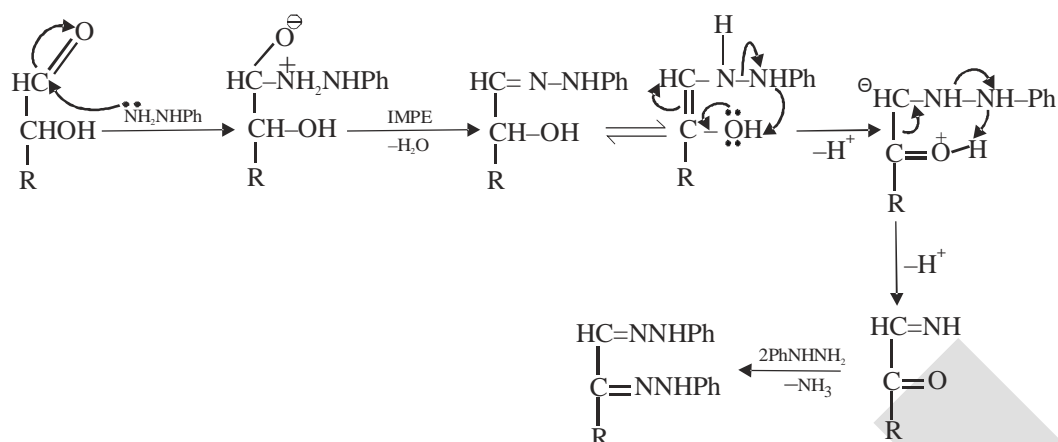
4. Reaction with NH<sub>2</sub>-OH (hydroxyl amine):

## 5. Reaction with phenyl hydrazine: Both glucose and fructose give "osazone".

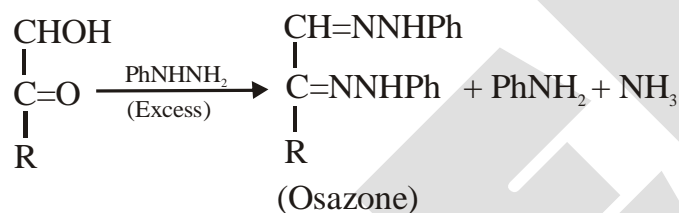
Reaction with glucose :



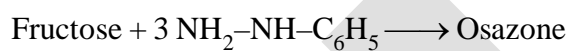
**Mechanism :**



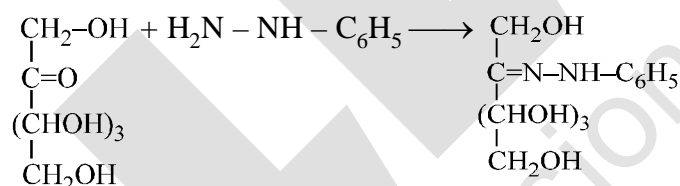
Propose Mechanism for :



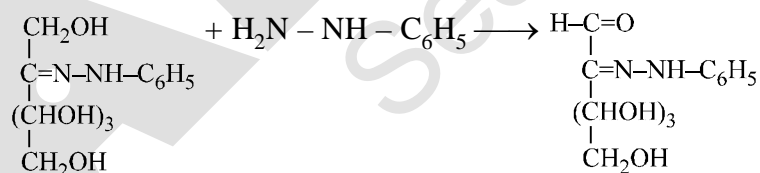
Reaction with fructose :



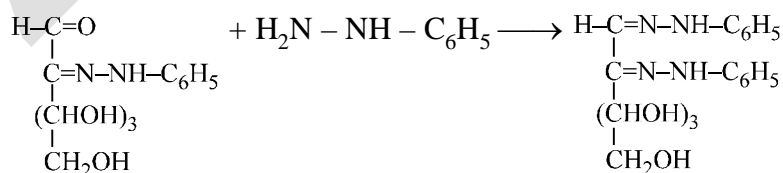
**Step (i)**



**Step (ii)**



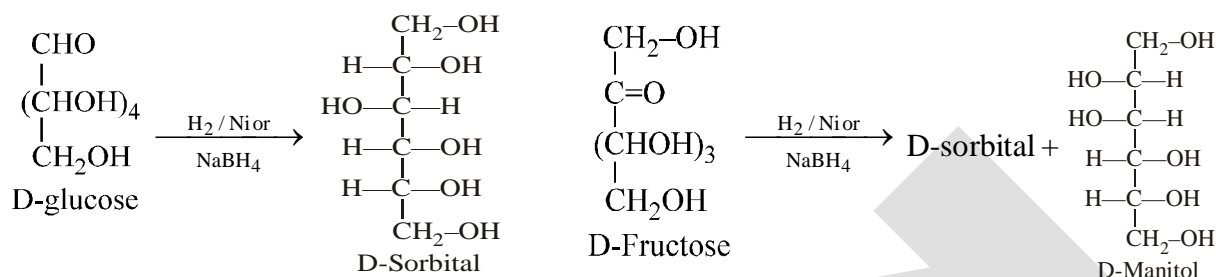
**Step (iii)**



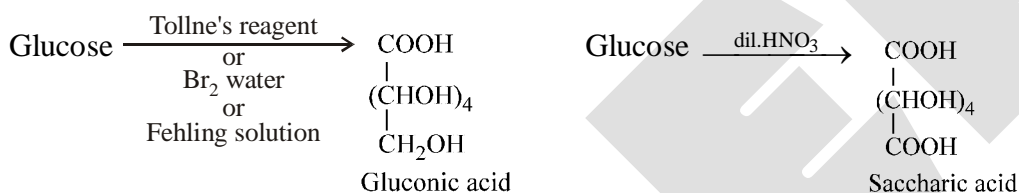
Glucose , Mannose & Fructose give same osazone because structure of last four carbons in these carbohydrates is same.

Only C-1 and C-2 in glucose and fructose are involved in osazone formation addition reaction do not run through out the chain. The failure to undergo further reaction has been explained by stabilization of the osazone by chelation.

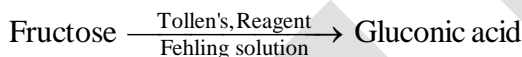
6. **Catalytic reduction:**



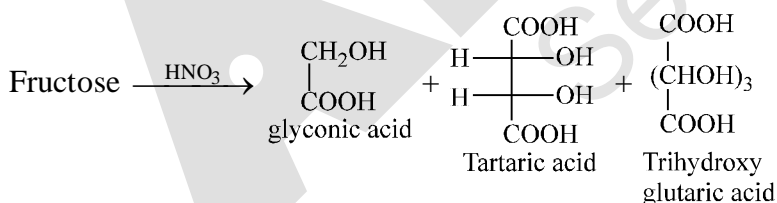
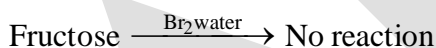
7. **Oxidation:**



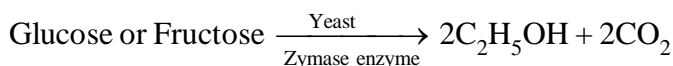
**Oxidation of fructose :**



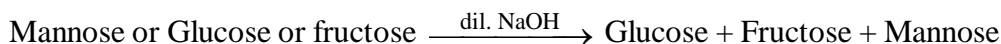
Fructose also reduces tollen's & fehling reagent because in basic medium fructose isomerises to glucose.



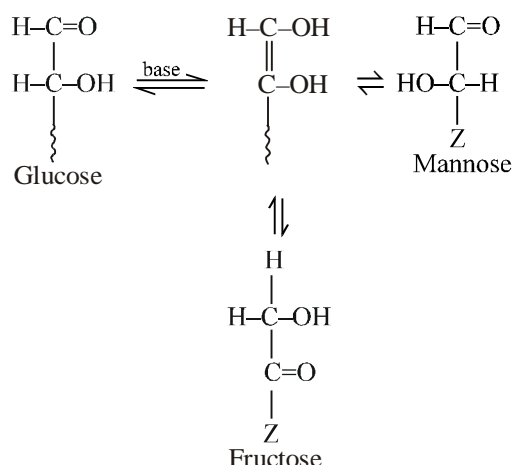
8. **Reaction with enzyme:**



9. **Reaction with dil NaOH / Ca(OH)<sub>2</sub>**

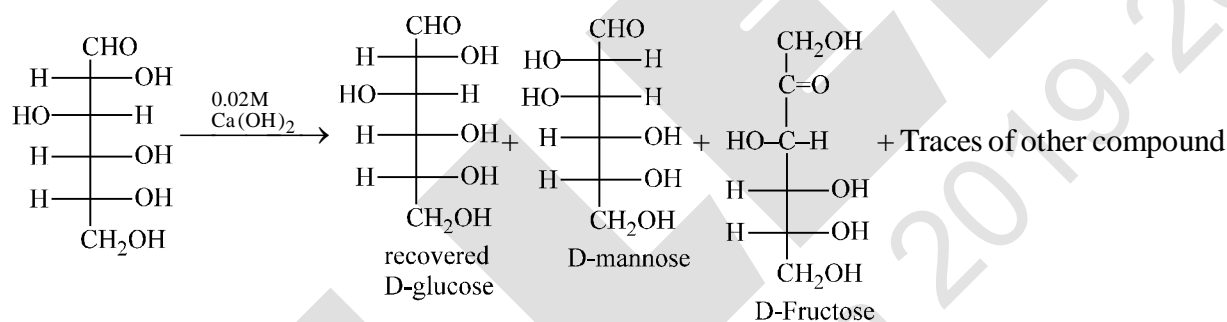


**Mechanism :**



**Base-catalyzed isomerisation of aldoses and Ketoses:**

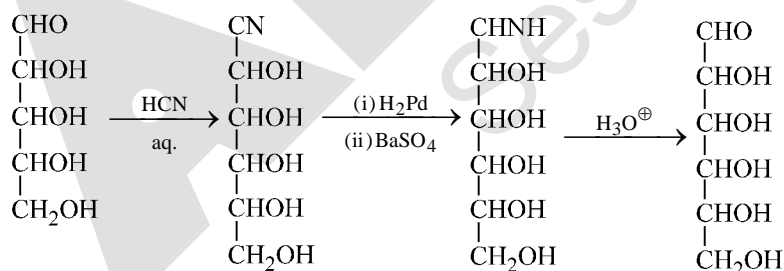
Although glucose in solution exists mostly in its cyclic hemiacetal forms it is also in equilibrium with a small amount of its acyclic aldehyde form.



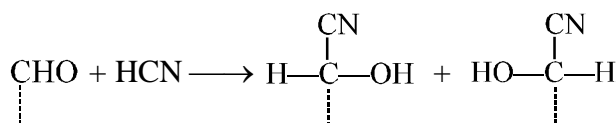
**Method of ascending the sugar series:**

An aldose may be converted into its next higher aldose eg. an aldopentose into an aldohexose.

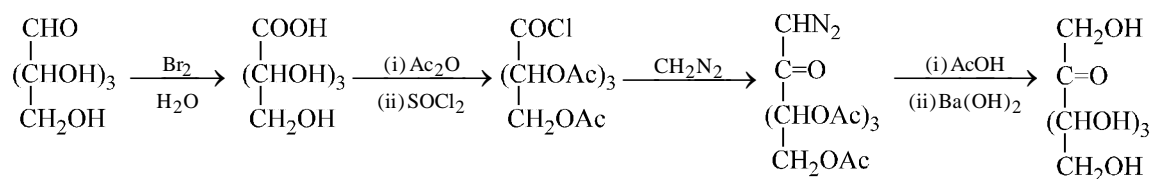
**By Kiliani Fischer upgradation:**



Theoretically two lactones are possible, since two cyanohydrin may be formed when hydrogen cyanide adds on to the aldopentose (a new asymmetrical carbon is produced)

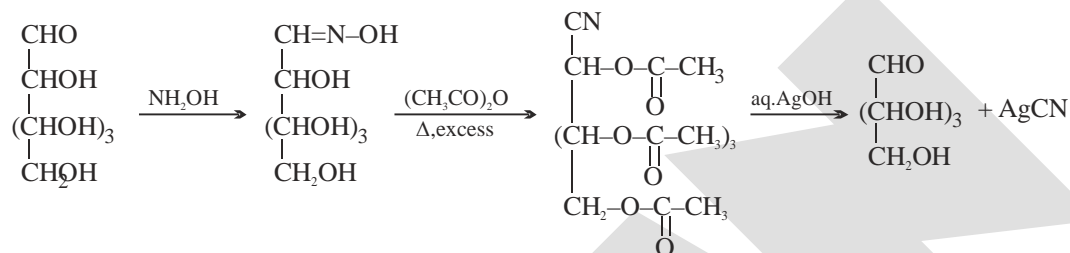


**Wolf from reaction :** Wolf from have stepped up an aldose to a ketose with one more carbon atom by a modified Arndt-Eistere reaction.

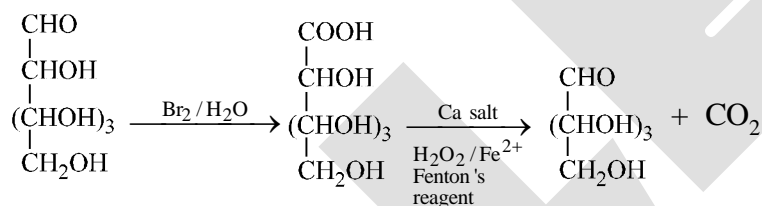


**Method of descending the sugar series :**

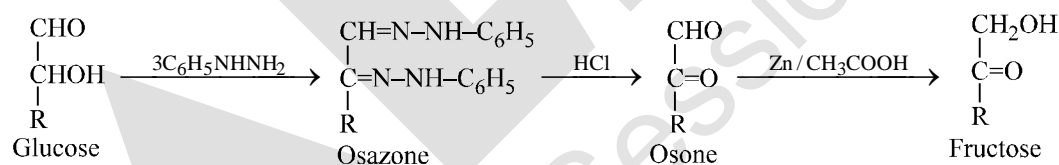
### Wohl's method:



### Ruff's method:

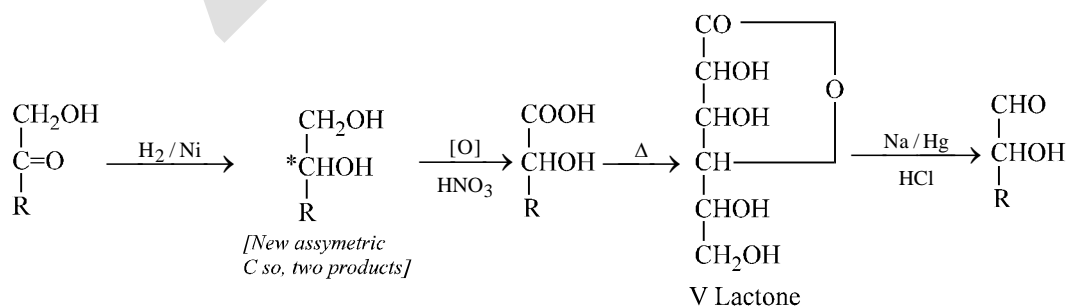


### Conversion of an aldose into a ketose :



An aldehyde group is reduced more readily than a ketonic group.

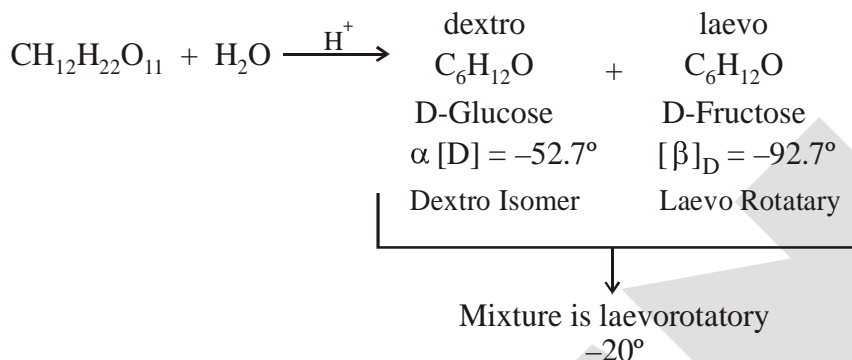
### Conversion of a Ketose into an aldose :



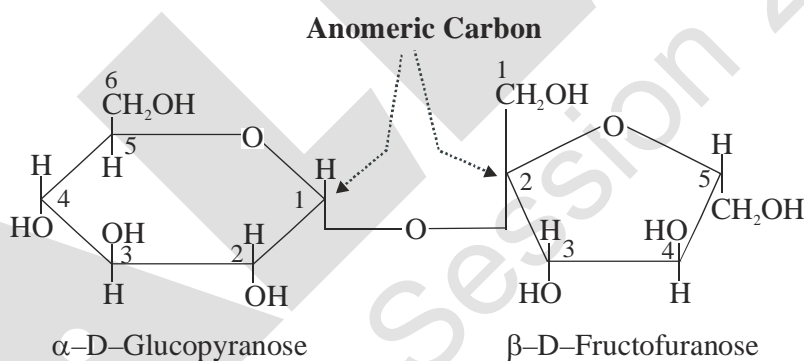
# SOME IMPORTANT CARBOHYDRATES

- Sucrose** ( $C_{12}H_{22}O_{11}$ ) : → A dimer of  $\alpha$ -D-Glucose &  $\beta$ -D-Fructose. It is white, crystalline & sweet substance soluble in water obtained from the sugar cane. When heated above its melting point. It forms a brown substance known as caramel.

It's aqueous solution is dextrorotatory  $[\alpha]_D = +66.5^\circ$

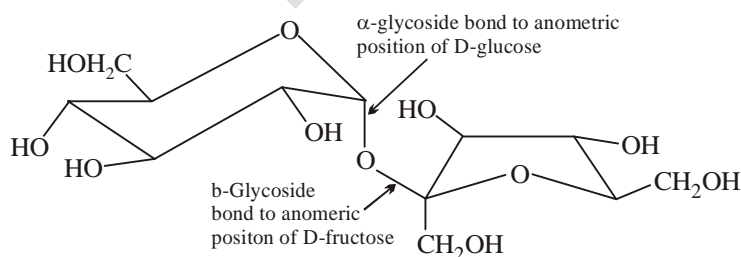


- Thus hydrolysis of sucrose brings about a change in the sign of rotation, from dextro (+) to leavo (−) & such a change is known as inversion of sugar and the mixture obtained on acidic hydrolysis is known as *invert sugar*.
- The inversion of cane-sugar may also be done by the enzyme invertase which is found in yeast.
- Sucrose is non-reducing sugar because it has stable acetal linkage & in aq. solution it does not give free carbonyl group and so it does not reduces Tollen's & Fehling's solution.
- This indicates that neither the aldehyde group of glucose nor the ketonic group of fructose is free in sucrose.

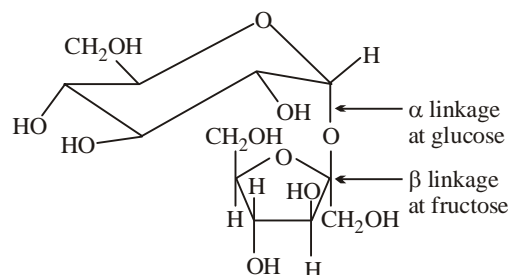


Structure of sucrose  
( $\alpha$ -D-glucopyranosyl- $\beta$ -D-fructofuranoside)

Do not show mutarotation .



**Fig. Showing Sucrose in other structure**

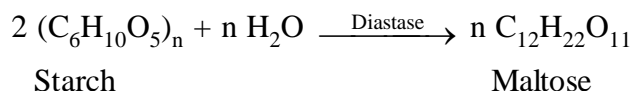


**Fig. Showing Sucrose in other structure**

2. Maltose :

- It is dimer of  $\alpha$ -D-Glucose

It is obtained by partial hydrolysis of starch by the enzyme diastase present in malt i.e., sprouted barely seeds.

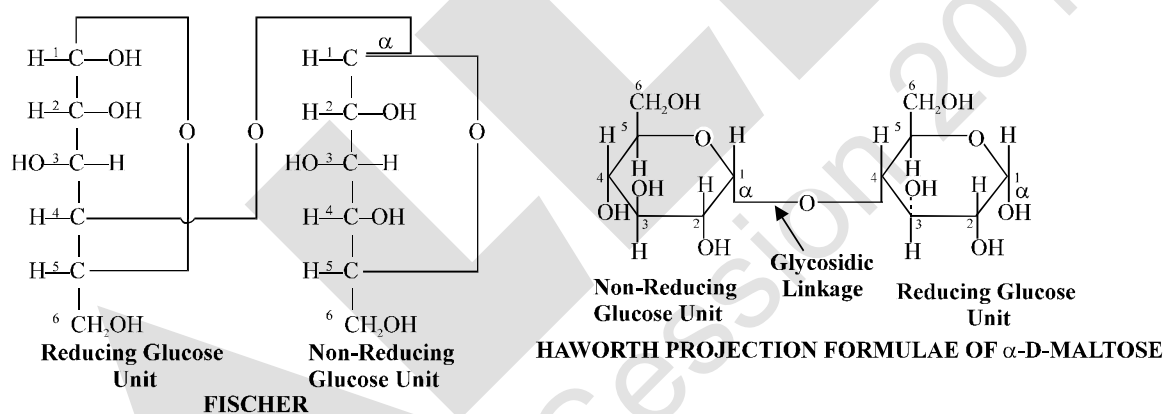


- Hydrolysis of one mole of maltose yields two moles of D-glucose.
- Maltose is a reducing sugar since it forms an osazone, undergoes mutarotation and also reduces Tollen's reagents and Fehling's solutions, Methylation studies have revealed that

(i) Both glucose units are present in the pyranose form.

(ii)  $\text{C}_1$  of one glucose unit is linked to  $\text{C}_4$  of the other

Further since maltose is hydrolysed by the enzyme maltase which specifically hydrolyses  $\alpha$ -glycosidic linkage, therefore, the non-reducing glucose unit in maltose must be present in the  $\alpha$ -form. In other words,  $\text{C}_1 - \alpha$  of non-reducing glucose unit is attached to  $\text{C}_4$  of the reducing glucose unit as shown in the figure on next page.

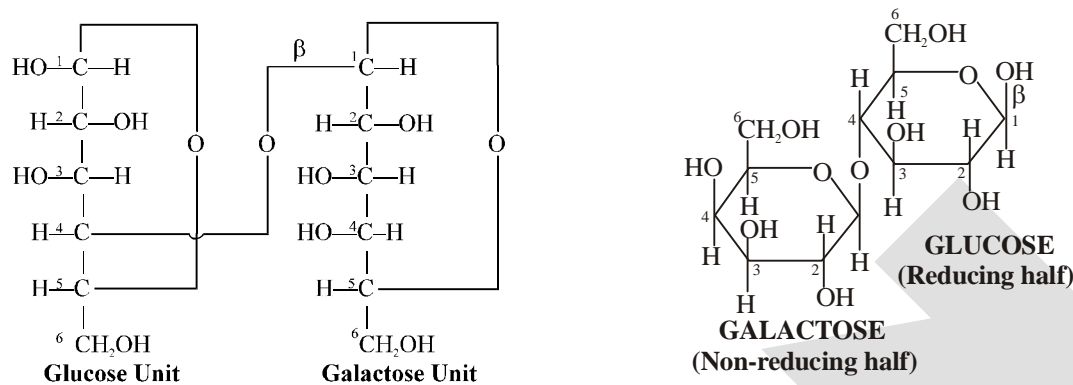
3. Lactose (Milk sugar)  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ 

Lactose occurs in milk and that is why it is called milk sugar.

Lactose on hydrolysis with dilute acid or by enzyme lactase, yields an equimolar mixture of D-glucose and D-galactose. It is a reducing sugar it forms an osazone, undergoes mutarotation and also reduces Tollen's or Fehling's solution. Methylation studies have revealed that

- both glucose and galactose are present in the pyranose form.
- glucose is the reducing half while  $\beta$ -galactose is the non-reducing half.
- $\text{C}_1$  of galactose unit is connected to  $\text{C}_4$  of glucose unit.

Further since emulsin, as, enzyme which specifically hydrolyses  $\beta$ -glycosidic linkages also hydrolyses lactose, therefore, galactose must be present in the  $\beta$ -form. In other words, in lactose,  $C_1 - \beta$  of galactose is attached to  $C_4$  of glucose as shown in figure.

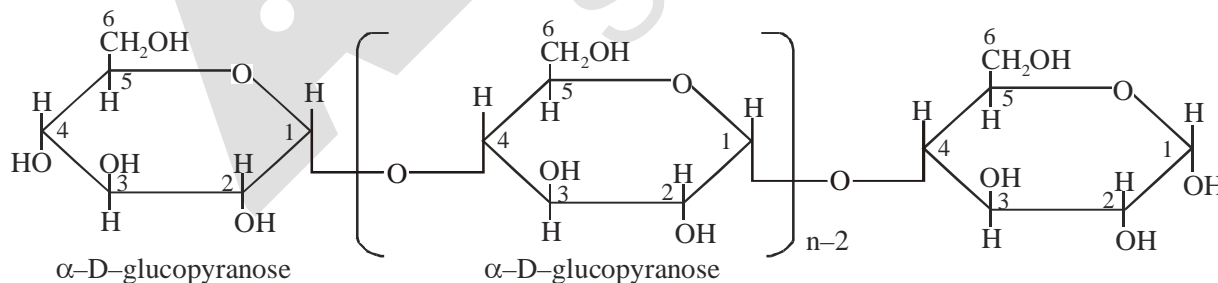


FISCHER

#### 4. Starch Amylum, $(C_6H_{10}O_5)_n$

**Occurrence :** The value of  $n$  (100 – 3000) generally however it may varies from source to source. It is the chief food reserve material or storage polysaccharide of plants and is found mainly in seeds, roots tubers wheat, maize, rice, potatoes, barley, bananas and sorghum are the main sources of starch. Starch occurs in the form of granules, which vary in shape and size depending upon their plant source.

Occurs in all green plants. Starch consists of two fractions, one being known as (amylose), which gives blue colour with iodine. This blue colour is believed to be due to the formation of an inclusion complex. An aqueous solution of  $\alpha$ -amylose slowly forms a precipitate, since  $\alpha$ -amylose has a strong tendency to 'revert' to the insoluble state in solution. Amylopectin is insoluble in water and is stable towards both hydrolysis to maltose by the enzyme diastase and to D(+)-glucose by dilute acids (amylopectin gives about 50 percent of maltose).

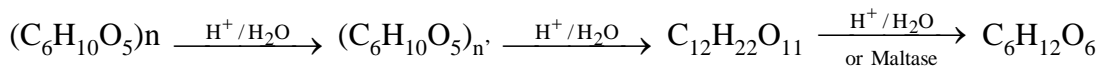


Structure of Starch ( $\alpha$ -D-glucoamylose)

$\alpha$ -amylose consists of an unbranched chain, with a molecular weight varying between 10,000( $n \approx 60$ ) and 10,00,000( $n \approx 6,000$ ), The value of  $n$  depends on the source and treatment of  $\alpha$ -amylose.



**Properties :** (i) Starch is a white amorphous powder sparingly soluble in water. Its aqueous solution gives a blue colour with iodine solution due to the formation of an inclusion complex. The blue pearls on cooling. (ii) On hydrolysis with dilute mineral acids or enzymes, starch breaks down first to smaller molecules ( $n > n'$ ), then to maltose and finally to D-glucose.



Starch

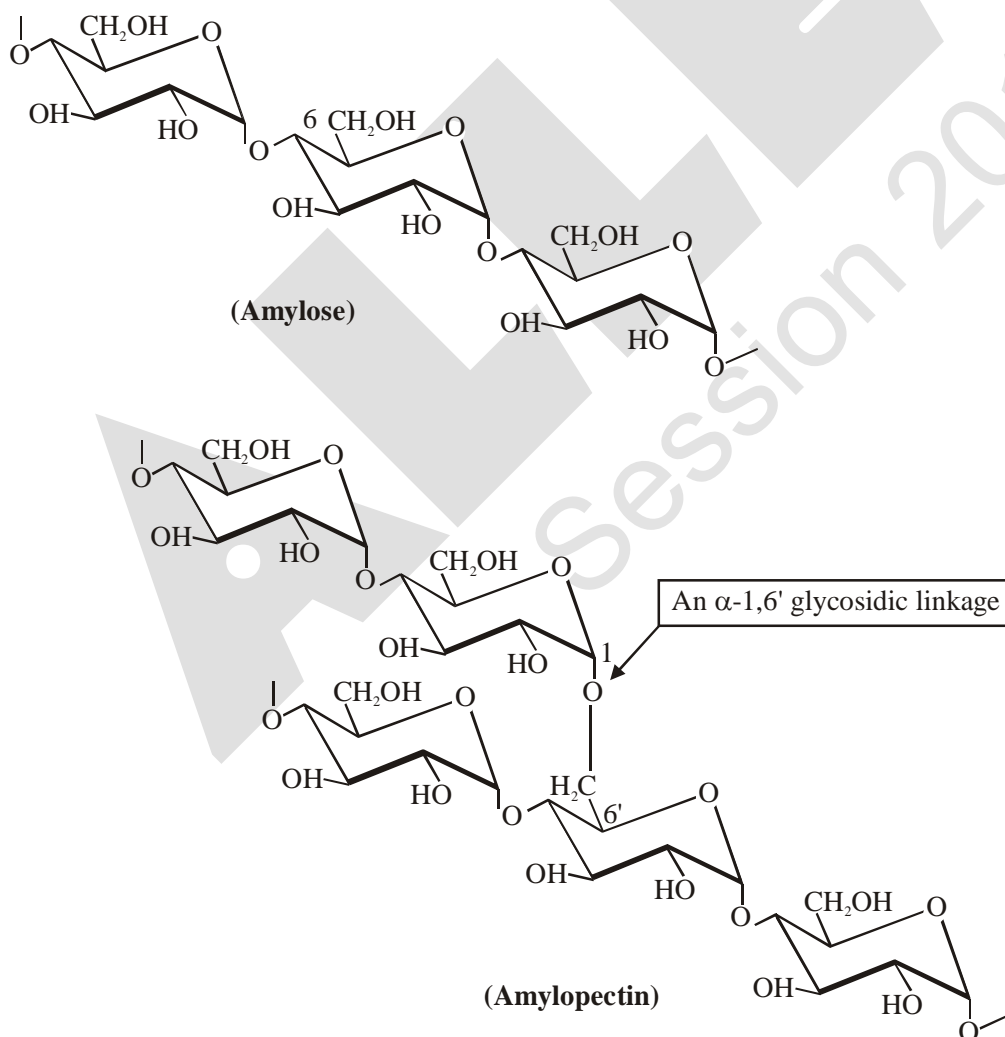
Maltose

D-Glucose

(iii) Starch is a non-reducing saccharide. It neither reduces Tollen's reagent or Fehling's solution nor forms an osazone. This suggests that all hemiacetal OH groups of glucose units at  $C_1$  are not free but are involved in glycosidic linkages.

**Composition :** Starch is not a single compound but is a mixture of two components—a water soluble component called amylose (10-20%) and a water insoluble component called amylopectin (80-90%). Both amylose and amylopectin are polymers of  $\alpha$ -D-glucose.

**Structure of amylose :** Amylose is water soluble and gives blue colour with iodine solution. It may have 100-3000 glucose units, i.e., its molecular mass can vary from 10,000 to 500,000. It is a linear polymer of  $\alpha$ -D-glucose in which  $C_1$  of one glucose unit is attached to  $C_4$  of the other through  $\alpha$ -glycosidic linkage as shown in figure.



### Pectins

Pectins are found in plant and fruit juices. Their characteristic property is the ability of their solutions to gelate, i.e. form jellies. They have a high molecular weight and are polygalacturonic acid (linked 1,4) with the carboxyl groups partially esterified with methanol.

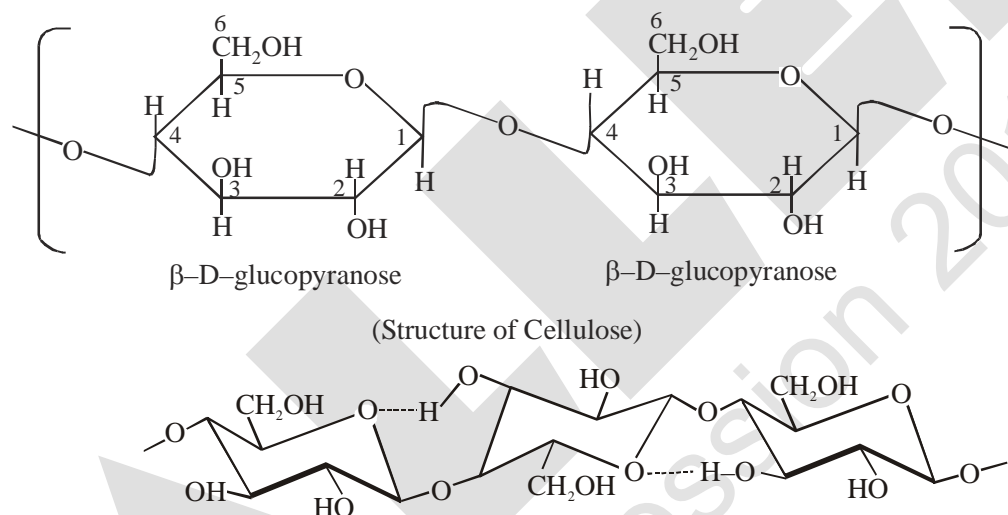
### Glycogen ( $C_6H_{10}O_5$ )<sub>n</sub> :

Glycogen is found in nearly all animals cells, occurring mainly in liver. It is the reserve carbohydrate of animals and so is often known as 'animal starch'. It has also been isolated from plant sources.

Glycogen is a white powder, soluble in water, the solution giving a purplish-red colour with iodine. On hydrolysis with dilute acid, glycogen gives D(+)-glucose. The molecular weight of glycogen has been given as 10,00,000 to 50,00,000 and glycogen contains highly branched chains. Glycogen has a structure similar to amylopectin, except that it has more cross-linking.

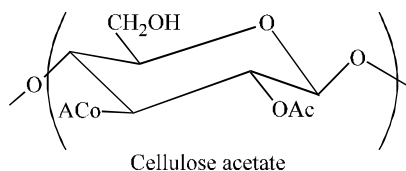
### 5. Cellulose:

Cellulose is colourless, solid which is insoluble in water & organic solvents. But it is soluble in ammoniacal cupric hydroxide (Schweizer's reagent) or in conc. HCl cellulose is a regular polymer of d-glucopyranose residues connected by  $\beta$ -1,4 glycosidic linkages. It is straight chain polymer.



#### Some points about cellulose :

1. General empirical formula ( $C_6H_{10}O_5$ )
2.  $\text{Cellulose} + \text{H}_2\text{O} \xrightarrow{\text{H}^+} 96\% \text{ of crystalline D-glucose}$
3. No. of monomer units in cellulose are 1000 – 1500 in one molecule.
4. Cellulose doesn't show mutarotation (like starch)
5. It is non reducing sugar because there is no hemiacetal linkage.
6. Acetylation, nitration & methylation of cellulose give trisubstituted cellulose which suggest that only three – OH groups are free.

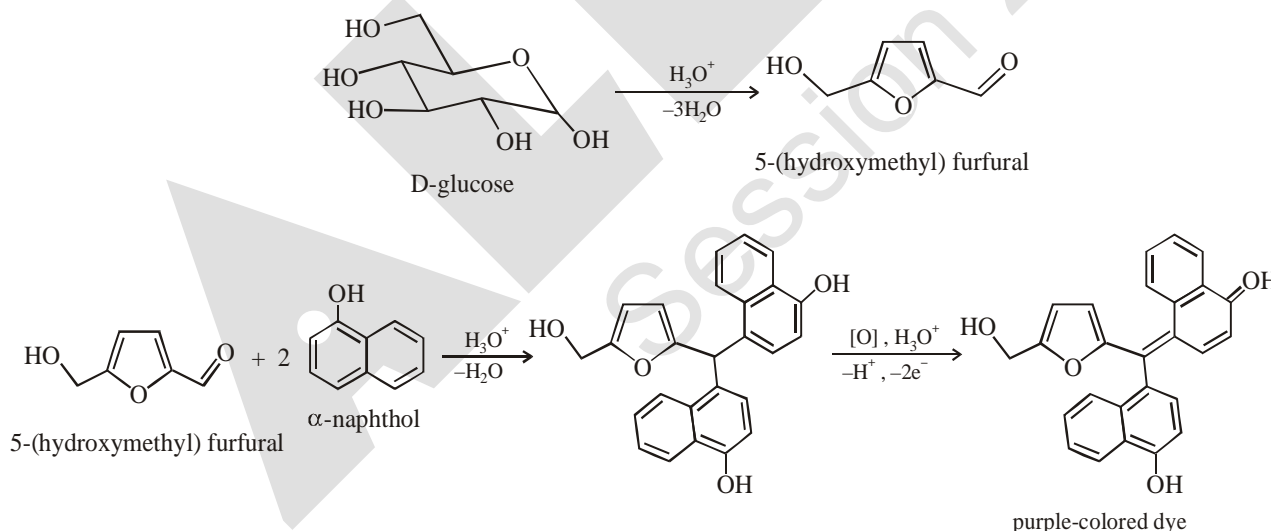


**Tests for carbohydrates:**

- (i) When heated in a dry test tube, it melts, turns brown and finally black, giving a characteristic smell of burning sugar.
- (ii) When warmed with a little concentrated  $\text{H}_2\text{SO}_4$ , it leaves a charred residue of carbon.
- (iii) **Molisch's Test** (named after Austrian botanist Hans Molisch) is a sensitive chemical test for the presence of carbohydrates, based on the dehydration of the carbohydrate by sulfuric acid to produce an aldehyde, which condenses with two molecules of phenol (usually  $\alpha$ -naphthol, though other phenols (e.g. resorcinol, thymol) also give colored products) resulting in a red- or purple-colored compound.

The test solution is combined with a small amount of Molisch's reagent ( $\alpha$ -naphthol dissolved in ethanol) in a test tube. After mixing, a small amount of concentrated sulfuric acid is slowly added down the sides of the sloping test-tube, without mixing, to form a bottom layer. A positive reaction is indicated by appearance of a purple ring at the interface between the acid and test layers.

All carbohydrates — monosaccharides, disaccharides, and polysaccharides — should give a positive reaction, and nucleic acids and glycoproteins also give a positive reaction, as all these compounds are eventually hydrolyzed to monosaccharides by strong mineral acids. Pentoses are then dehydrated to furfural, while hexoses are dehydrated to 5-hydroxymethylfurfural. Either of these aldehydes, if present, will condense with two molecules of naphthol to form a purple-colored product, as illustrated below by the example of glucose:

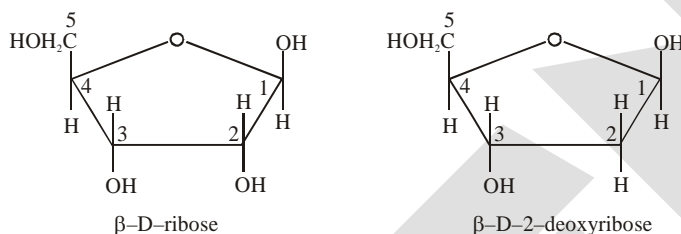


## NUCLEIC ACIDS

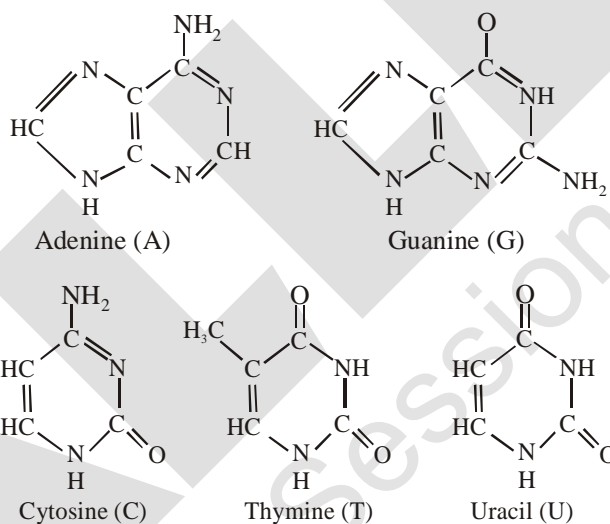
The particles in nucleus of the cell, responsible for heredity, are called chromosomes which are made up of proteins and another type of biomolecules called **nucleic acids**. These are mainly of two types, the **deoxyribonucleic acid (DNA)** and **ribonucleic acid (RNA)**. Since nucleic acids are long chain polymers of **nucleotides**, so they are also called polynucleotides.

### Chemical Composition of Nucleic Acids

Complete hydrolysis of DNA (or RNA) yields a pentose sugar, phosphoric acid and nitrogen containing heterocyclic compounds (called bases). In DNA molecules, the sugar moiety is  $\beta$ -D-2-deoxyribose whereas in RNA molecule, it is  $\beta$ -D-ribose.

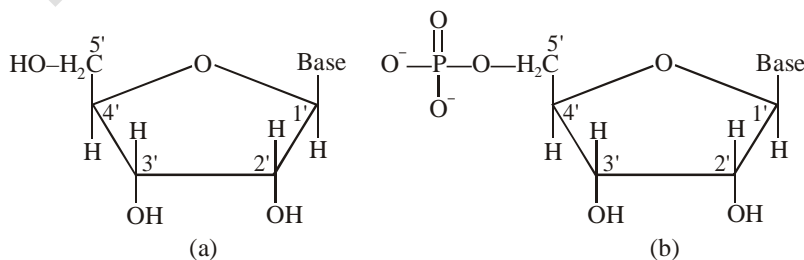


DNA contains four bases viz. adenine (A), guanine (G), cytosine (C) and thymine (T). RNA also contains four bases, the first three bases are same as in DNA but the fourth one is uracil (U).



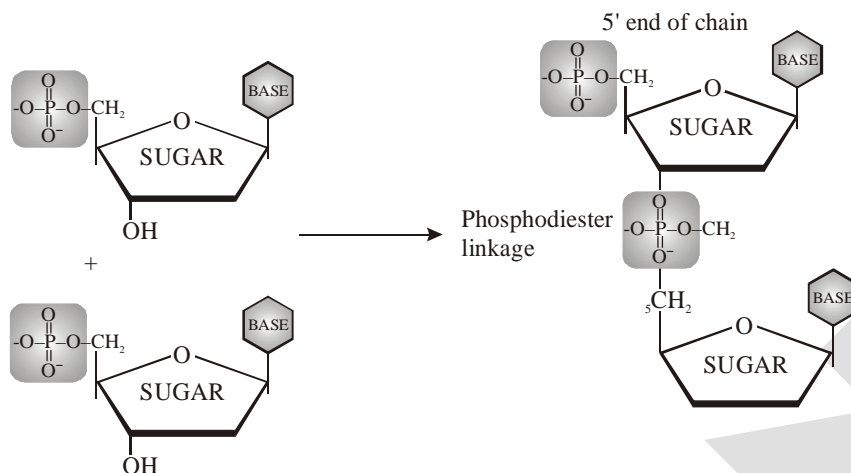
### Structure of Nucleic Acids

A unit formed by the attachment of a base to 1' position of sugar is known as **nucleoside**. In nucleosides, the sugar carbons are numbered as 1', 2', 3', etc. in order to distinguish these from the bases. When nucleoside is linked to phosphoric acid at 5'-position of sugar moiety, we get a nucleotide



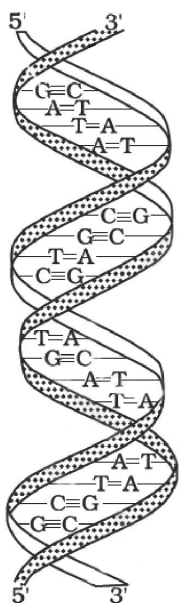
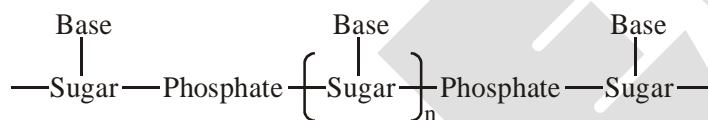
Structure of (a) a nucleoside and (b) a nucleotide

Nucleotides are joined together by phosphodiester linkage between 5' and 3' carbon atoms of the pentose sugar. The formation of a typical dinucleotide is shown in Fig.



### Formation of dinucleotide

A simplified version of nucleic acid chain is as shown below.

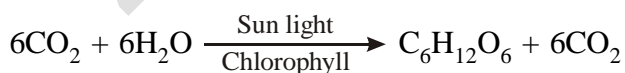


Information regarding the sequence of nucleotides in the chain of a nucleic acid is called its primary structure. Nucleic acids have a secondary structure also. James Watson and Francis Crick gave a double strand helix structure for DNA (Fig. 14.7). Two nucleic acid chains are wound about each other and held together by hydrogen bonds between pairs of bases. The two strands are complementary to each other because the hydrogen bonds are formed between specific pairs of bases. Adenine forms hydrogen bonds with thymine whereas cytosine forms hydrogen bonds with guanine.

In secondary structure of RNA, helices are present which are only single stranded. Sometimes they fold back on themselves to form a double helix structure. RNA molecules are of three types and they perform different functions. They are named as **messenger RNA (m-RNA)**, **ribosomal RNA (r-RNA)** and **transfer RNA (t-RNA)**.

**Fig. : Double strand helix structure for DNA**

### Photosynthesis



\* 3 ATP are required to fix 1 mole of  $\text{CO}_2$ . Therefore 18 ATP are required to fix 6 mole of  $\text{CO}_2$ .

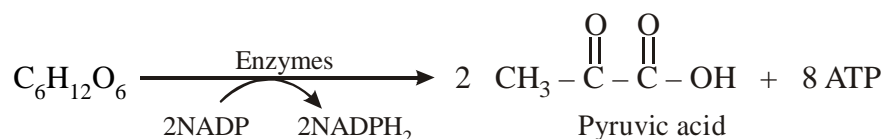
### Cellular Respiration



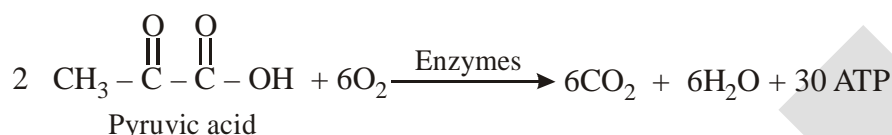
\* 38 ATP are generated by complete oxidation of 1 mole of glucose. But net gain of ATP are 36, because 2 ATP are consumed when pyruvic acid enters mitochondria.

\* Complete oxidation takes place in two steps

**Step - 1 : Glycolysis or EMP or HMP (Completes in cytoplasm)**



**Step - 2 : Kreb cycle (Completes in mitochondria)**

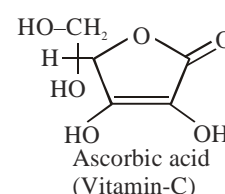


### VITAMINES

**Table : Some important Vitamins, their Sources and their Deficiency Diseases**

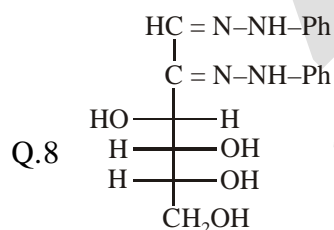
| Sl. No. | Name of Vitamins                       | Sources                                                 | Deficiency diseases                                                                                        |
|---------|----------------------------------------|---------------------------------------------------------|------------------------------------------------------------------------------------------------------------|
| 1       | Vitamin A                              | Fish liver oil, carrots, butter and milk                | Xerophthamla (hardening of cornea of eye) Night blindness                                                  |
| 2       | Vitamin B <sub>1</sub> (Thiamine)      | Yeast, milk, green vegetables and cereals               | Beri beri (loss of appetite, retarded growth)                                                              |
| 3       | Vitamin B <sub>3</sub> (Riboflavin)    | Milk, eggwhite, liver, kidney                           | Cheilosis (fissuring at corners of mouth and lips), digestive disorders and burning sensation of the skin. |
| 4       | Vitamin B <sub>3</sub> (Pyridoxine)    | Yeast, milk, egg yolk, cereals and grams                | Convulsions                                                                                                |
| 5       | Vitamin B <sub>12</sub>                | Meat, fish, egg and curd                                | Pernicious anaemia (RBC deficient in haemoglobin)                                                          |
| 6       | Vitamin B <sub>5</sub> (Ascorbic acid) | Citrus fruits, amla and green leafy vegetables          | Scurvy (bleeding gums)                                                                                     |
| 7       | Vitamin D                              | Exposure to sunlight, fish and egg yolk                 | Rickets (bone deformities in children) and osteomalacia (soft bones and joint pain in adults)              |
| 8       | Vitamin E                              | Vegatable oils like wheat germ oil, sunflower oil, etc. | Increased fragility of RBCs and muscular weakness                                                          |
| 9       | Vitamin K                              | Green leafy vegetables                                  | Increased blood clotting time                                                                              |

**NOTE :** Vitamin-D , E , K , A are fat soluble vitamins.  
Vitamin-B , C are water soluble vitamins.



## EXERCISE # I

- Q.1 Iso-electric point of alanine is (pH = 6). At which pH, maximum concentration of zwitter ion of alanine will be present ?  
 (A) pH > 6 (B) pH < 6 (C) pH = 6 (D) pH = 7
- Q.2 At iso-electric point :  
 (A) Concentration of cation is equal to concentration of anion  
 (B) Net charge is zero  
 (C) Maximum conc. of di-pole ion (Zwitter ion) will be present  
 (D) All of the above
- Q.3 Which of following amino acid has lowest iso-electric point ?  
 (A) Glycine (B) Alanine (C) Aspartic acid (D) Lysine
- Q.4  $\text{H}-\text{C}\equiv\text{C}-\text{H} \xrightarrow[\text{H}_2\text{SO}_4]{\text{HgSO}_4} (\text{A}) \xrightarrow[(2) \text{H}_3\text{O}^+]{(1) \text{NH}_3+\text{HCN}} (\text{B})$  ; Product (B) of given reaction is :  
 (A) Glycine (B) Alanine (C) Valine (D) Leucine
- Q.5 Which amino acid does not contain chiral centre ?  
 (A) Valine (B) Leucine (C) Glycine (D) Iso-leucine
- Q.6 Which of the following is Sanger reagent ?  
 (A) 2,4-Di-nitro fluorebenzene (B) Phenyl isocyanane  
 (C) 2,4-Di-nitro chlororbenzene (D) 12,4-Di-nitro-iodobenzene
- Q.7 A D-carbohydrate is :  
 (A) Always dextrorotatory  
 (B) Always laevorotatory  
 (C) Always the mirror of the corresponding L-carbohydrate  
 (D) None of these



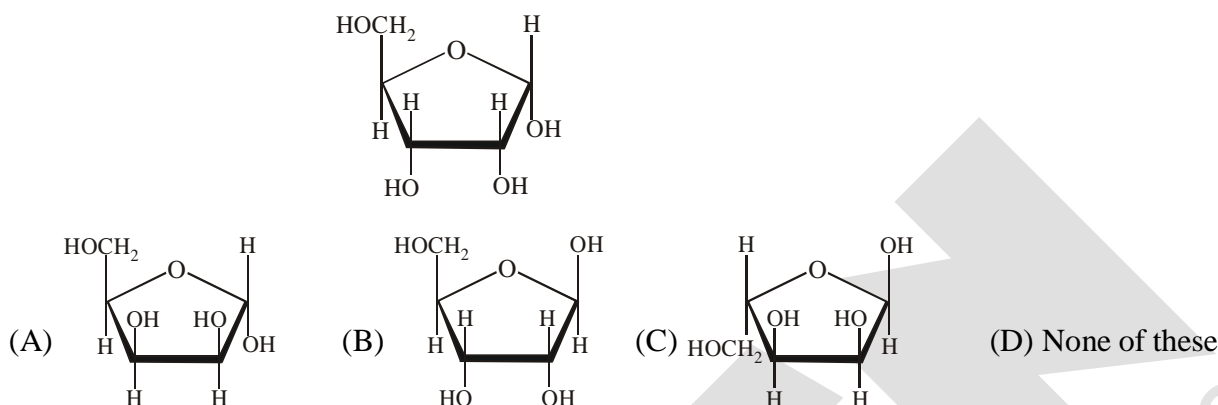
The given osazone can be obtained by :

- (A) D-glucose (B) D-mannose (C) D-Idose (D) Both (A) & (B)

Q.9 Which of the following pair gives same phenyl osazone ?

- (A) D-Glucose and D-Allose (B) D-Glucose and D-Altrose  
(C) D-Glucose and D-Mannose (D) D-Glucose and D-Talose

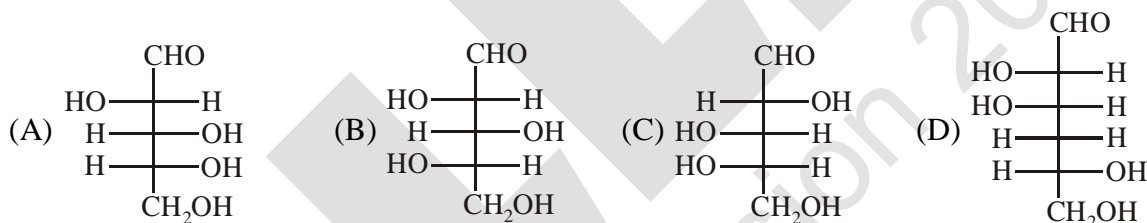
Q.10 Which of the following represents the anomer of the compound shown ?



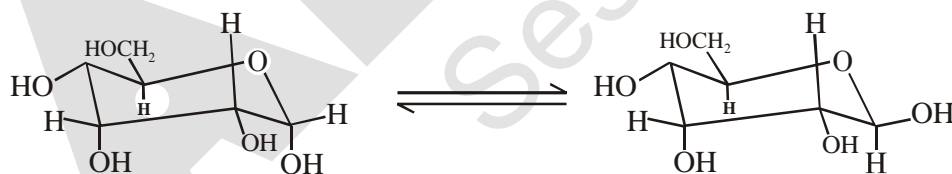
Q.11 For the complex conversion of D-glucose into the corresponding osazone, the minimum number of equivalents of phenyl hydrazine required is :

- (A) Two (B) Three (C) Four (D) Five

Q.12 Which of the following structure is L-arabinose ?



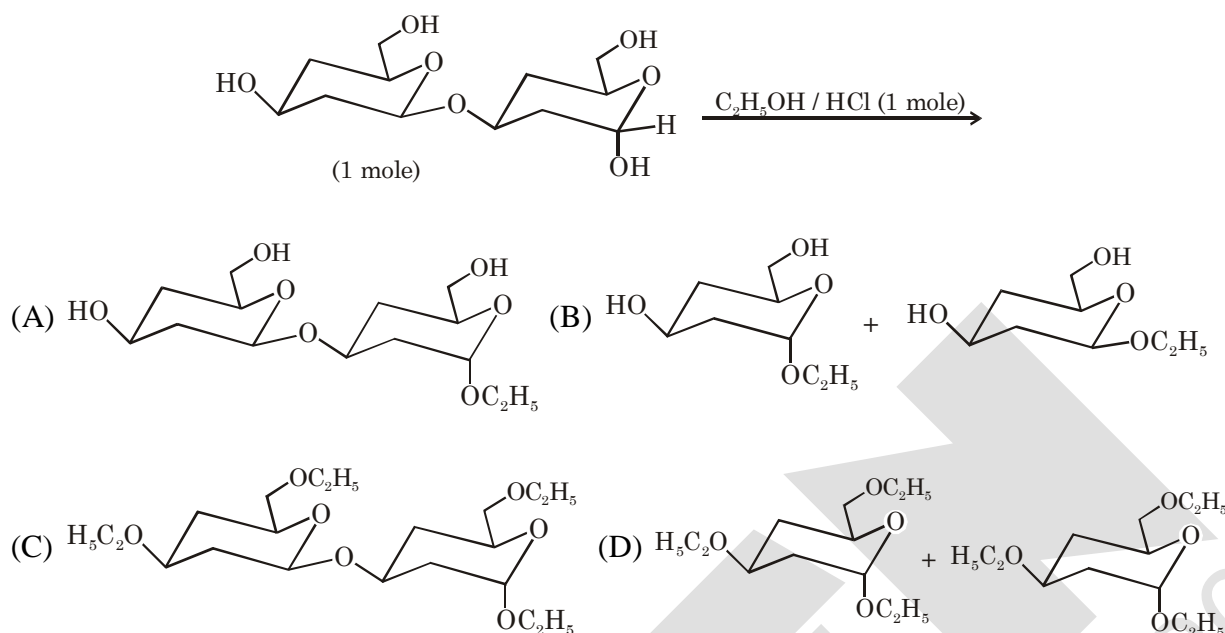
Q.13 Which one of the statements concerning the equilibrium shown is true ?



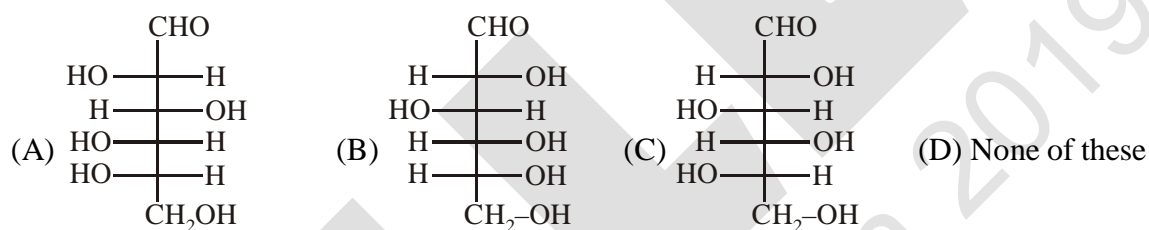
- (A) The two structures are enantiomers of each other. They have equal but opposite optical rotations and racemize slowly at room temperature  
(B) The two structures are enantiomers of each other. They racemize too rapidly at room temperature for their optical rotations to be measured  
(C) The two structures are diastereomers of each other. Their interconversion is called mutarotation  
(D) The two structures are diastereomers of each other. Their interconversion does not require breaking and making bonds, only a change in conformation



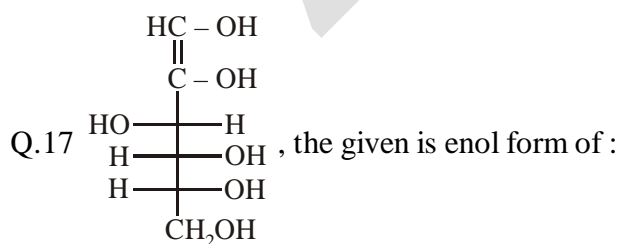
Q.14 Major product of following reaction is :



Q.15 What is the structure of L-glucose ?



Q.16 What is the structure of L-glyceraldehyde ?



- (A) D-glucose      (B) D-mannose      (C) D-fructose      (D) All of these

Q.18 D-glucose & D-fructose can be differentiated by :

- (A) Fehling solution      (B) Tollen's reagent      (C) Benedict test      (D)  $\text{Br}_2 / \text{H}_2\text{O}$

Q.19 D-Glucose exist in x different forms. The value of x (stereoisomer) is :

- (A) 2      (B) 3      (C) 4      (D) 5

Q.20  $\text{D-Mannose} \xrightleftharpoons{\text{HO}^-} \text{D-Glucose} \xrightleftharpoons{\text{HO}^-} \text{(A)}$  ;

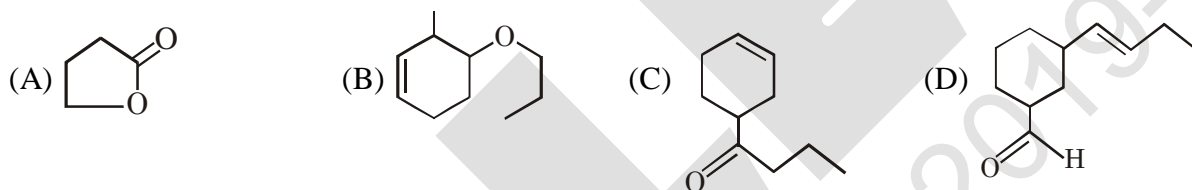
Product (A) of above reaction is :

- (A) D-glucose      (B) D-fructose      (C) D-talose      (D) D-idose

Q.21 Which of the following statement is not correct for maltose.

- (A) It is a disaccharide      (B) It undergoes mutarotation  
(C) It is a reducing sugar      (D) It does not have hemiacetal group.

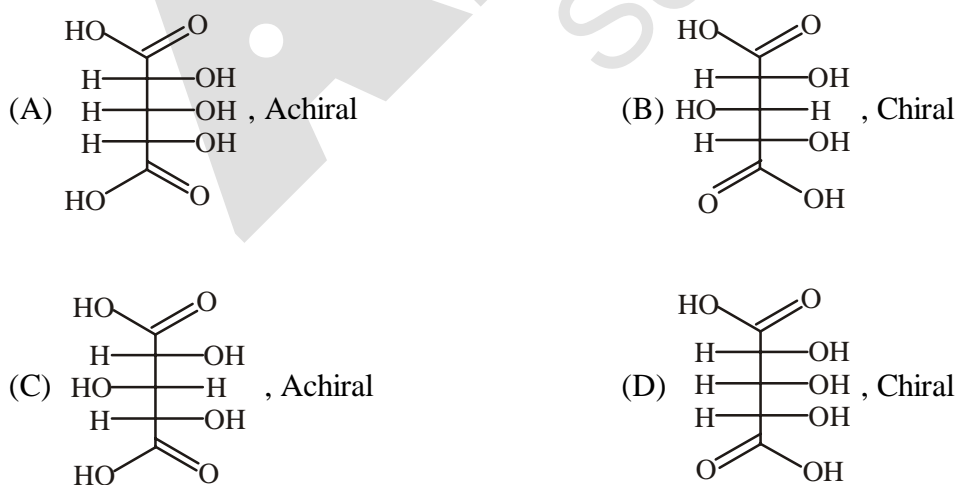
Q.22 A compound which does not react with Brady's reagent but decolourise  $\text{Br}_2 / \text{H}_2\text{O}$  solution is :



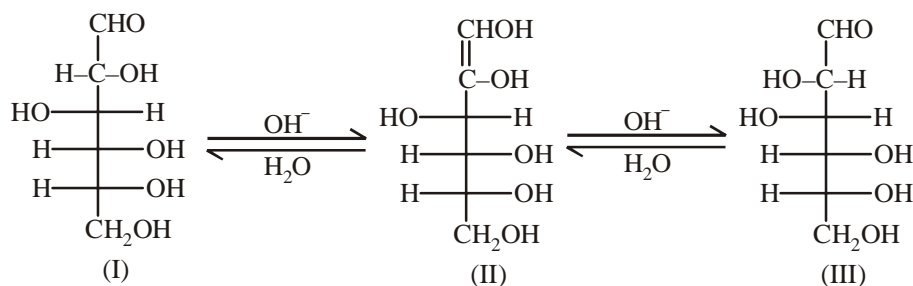
Q.23 Maltose is made up of to two sugars—

- (A) Glucose      (B) Fructose  
(C) Glucose & galactose      (D) Glucose & fructose

Q.24 D-Ribose when treated with dilute  $\text{HNO}_3$  forms.



Q.25 Consider the given process



and identify the incorrect statement.

- (A) Configuration at C-2 is lost on enolisation  
 (B) I and III are epimers  
 (C) Proton transfer from water to C-1 converts ene diol to an aldose.  
 (D) D-glucose can isomerise to D-fructose through enol intermediate.

Q.26 When methyl D-glucopyranoside is treated with  $\text{HIO}_4$  its number of mole consumed per mole of the sugare is -

- (A) 2 (B) 3 (C) 4 (D) 5

Q.27  $\alpha$  - amino acid when heated with  $\text{NaOH}/\text{CaO}$  forms -

- (A)  $\alpha, \beta$  - unsaturated acid (B)  $\alpha, \beta$  - unsaturated amine  
 (C) Carboxylic acid (D) Amine

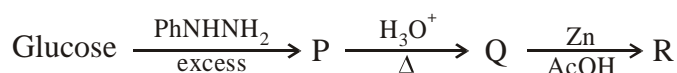
Q.28 The configuration of the C-2 epimer of D-glucose is-

- (A) 2R, 3S, 4R, 5S (B) 2S, 3S, 4R, 5R  
 (C) 2S, 3R, 4S, 5R (D) 2R, 3S, 4R, 5R

Q.29 Mutarotation involve-

- (A) Racemisation (B) Diastereomerisation  
 (C) Optical resolution (D) Conformational inversion

Q.30 Consider the reaction sequence -



The product R is -

- (A) Arbinose (B) Sorbitol (C) Fructose (D) Mannose

Q.31 The pH of the solution containing following zwitter ion species is  $\text{NH}_3^+ - \text{C}(\text{COO}^-)(\text{H})(\text{R})$

- (A) 4 (B) 5 (C) 7 (D) 9

Q.32 Peptide linkage is -

- (A)  $\text{O}=\text{C}-\text{O}-$  (B)  $\text{O}=\text{C}-\text{NH}_2$  (C)  $\text{O}=\text{C}-\text{NH}-$  (D)  $\text{O}=\text{C}-\text{NH}-\text{NH}_2$

Q.33 Same osazone derivative is obtained in case of D-glucose, D-Mannose and D-Fructose due to

- (A) The same configuration at C-5  
(B) The same constitution.  
(C) The same constitution at C-1 and C-2  
(D) The same constitution and acid configuration at C-3, C-4, C-5 and C-6 but different constitution and configuration at C-1 and C-2 which becomes identical by osazone formation.

Q.34  $\text{D}(-)\text{-Erythrose} \xrightarrow{\text{NaBH}_4} (\text{P})$   
 $\text{D}(-)\text{-Threose} \xrightarrow{\text{NaBH}_4} (\text{R})$

Which of the following statement is correct about P and R ?

- (A) Both are optically active (B) Both are optically inactive  
(C) P is optically inactive and R is optically active (D) Neither P nor R has asymmetric carbon.

Q.35 The monomer of nucleic acids are held together by

- (A) Phosphodiester linkage (B) Amide linkage  
(C) Glycosidic linkage (D) Ester linkage

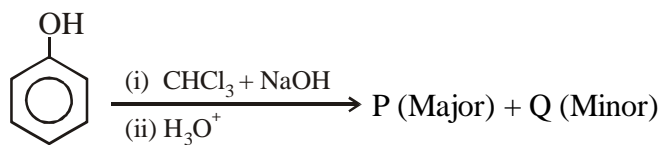
Q.36 Select the incorrect statement about Nylon 2-nylon-6.

- (A) It is a copolymer  
(B) It is biodegradable  
(C) It is an alternating polyamide  
(D) It is made up of  $\text{CH}_3-\text{CH}(\text{NH}_2)-\text{COOH}$  and  $\text{H}_2\text{N}(\text{CH}_2)_5\text{COOH}$

Q.37 The monomer that can undergo radical, cationic and anionic polymerisation with equal ease-

- (A)  $\text{Me}-\text{C}(\text{Me})=\text{CH}_2$  (B)  $\text{Ph}-\text{CH}=\text{CH}_2$  (C)  $\text{CH}_2=\text{CH}_2$  (D)  $\text{CH}_2=\text{CH}-\text{CN}$

Q.38 Consider the reaction-



Mixture of A and B can be best separated by -

- (A) Steam distillation (B) Vacuum distillation  
(C) Fractional distillation (D) Crystallisation

Q.39 Which of the following statements are incorrect :

- (A) Copolymer of 1,3-butadiene & acrylonitrile is Buna-S  
(B) HDPE is obtained by Ziegler-Natta polymerisation  
(C) Polymer dacron can be polyester fabric  
(D) Phenol & formaldehyde resin is called novolac

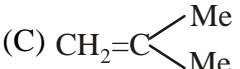
Q.40 A segment (X) of cellulose obtained on partial hydrolysis has molecular mass 1476 gm. On complete acidic hydrolysis, mass of the product obtained is 1620 gm. Find out the number of glycosidic linkage(s) present in segment (X) :

- (A) 8 (B) 6 (C) 4 (D) 10

Q.41 When solidum extract is treated with  $\text{FeCl}_3$  solution a blood red coloured is obtained due to the presence of -

- (A)  (B)   
(C)  (D) 

Q.42 The monomer that undergo radical polymerisation most easily is

- (A)  $\text{CH}_2=\text{CH}_2$  (B)  $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$  (C)  (D)  $\text{CH}_3-\text{CH}=\text{CH}_2$

## EXERCISE # II

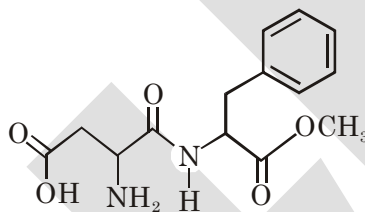
Q.1 Carbohydrates may be :

- (A) Sugars (B) Starch  
(C) Polyhydroxy aldehyde/ ketones (D) Compounds that can be hydrolysed to sugar

Q.2 Select the correct statement :

- (A) Glycosides do not undergo mutarotation  
(B) All OH groups of a cyclic monosaccharides are converted to ethers by treatment with base and an alkyl halide  
(C)  $\alpha$ -D glucose reacts with  $\text{Ag}_2\text{O}$  and excess  $\text{CH}_3\text{I}$  to form tetramethyl ether  
(D) D-glucose upon treatment with warm  $\text{HNO}_3$  forms D-glucaric acid

Q.3 "Aspartame" is roughly 100 times as sweet as cane sugar. On complete hydrolysis of aspartame, products obtained is/are :



- (A)  $\text{PhCH}_2\text{—CH(NH}_2\text{)—CO}_2\text{H}$  (B)  $\text{H}_2\text{N—CH(CH}_2\text{CO}_2\text{H)—CO}_2\text{H}$  (C)  $\text{CH}_3\text{OH}$  (D)  $\text{CH}_3\text{—CH(NH}_2\text{)—CO}_2\text{H}$

Q.4 Starch molecules are polymer with repeating glucose units. Select the correct statement(s).

- (A) Glucose units are joined through  $\alpha$ -glycosidic linkage  
(B) The branches of amylopectin are linked to the chain with  $\alpha$ -1,6'-glycosidic linkages  
(C) The linear linkages of amylopectin are formed by  $\alpha$ -1,6'-glycosidic bond  
(D) Amylose has an unbranched skeleton of glucose molecules with  $\alpha$ -1,4'-glycosidic linkages

Q.5 Select the correct option.

- (A) Isoelectric point is the pH at which an amino acid exists primarily in its neutral form.  
(B) Isoelectric point is the average of  $\text{pK}_a$  values of  $\alpha$ -COOH amino  $\alpha$ -  $\text{NH}_3^+$  groups [ valid only for neutral amino acid ]  
(C) Glycine is characterised by two  $\text{pK}_a$  values  
(D) For neutral amino acid the concentration of zwitter ion is maximum at its isoelectric point

Q.6 Amino acids are synthesised from

- (A)  $\alpha$ -Halo acids by reaction with  $\text{NH}_3$
- (B) Aldehydes by reaction with  $\text{NH}_3$  and cyanide ion followed by hydrolysis
- (C) Pyruvic acid is treated with  $\text{NH}_3$  followed by addition of  $\text{H}_2(\text{Ni})$
- (D) Alcohols by reaction with  $\text{NH}_3$  and  $\text{CN}^-$  ion followed by hydrolysis.

Q.7 Which of the following carbohydrates develops blue colour on treatment with iodine solution ?

- (A) Glucose
- (B) Amylose
- (C) Starch
- (D) Fructose

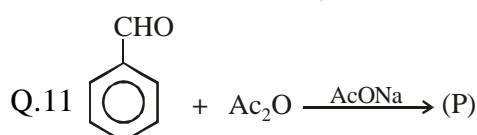
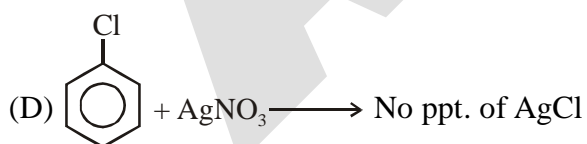
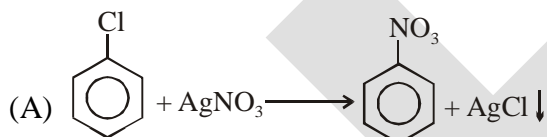
Q.8 Select the **correct** statement

- (A) High density polythene is a linear polymer.
- (B) Low density polythene is a branched chain polymer.
- (C) Chain growth polymers are also known as addition polymer.
- (D) Step growth polymer is also known as condensation polymer.

Q.9 Select the correct statement.

- (A) Elastomers have the weakest intermolecular forces
- (B) Buna-N is example of synthetic copolymer
- (C) Some fibres have crystalline nature
- (D) Thermoplastic polymers have stronger intermolecular forces than fibres

Q.10 Which of the following options are correct :



Before isolating (P) unreacted  $\text{Ph-CHO}$  is removed first. Select the correct statement.

- (A) P is cinnamaldehyde
- (B) P is crotonic acid
- (C) Removal is done by simple distillation
- (D) P is cinnamic acid.

Q.12 If on a strand of DNA the base sequence is ATTGACGCAT then the sequence transcription on RNA would be -

- (A) UAACUGCGUA (B) AUUCUGCGUA  
(C) UAACTGCGUA (D) TAACTGCGTA

Q.13 Select the correct statement among following

- (A) Number of chiral atom in  $\alpha$ -D-glucose is less than D-glucose  
(B) D-glucose and D-fructose give same product with  $\text{HIO}_4$   
(C) D-glucose and D-fructose give same product with  $\text{H}_2\text{NOH}$   
(D) D-glucose and D-fructose form same product with  $\text{H}_2\text{N}-\text{NH}-\text{Ph}$

Q.14 The N-base which differentiate DNA with RNA is :

- (A) Cytosine (B) Uracil (C) Adenine (D) Guanine

Q.15 Correct statement

- (A) Nylon-66 is example of addition polymer  
(B) Alanin having pH 9 at isoelectric point  
(C) Fructose when reacts with fehling solution reddish brown ppt. formed  
(D) All of these

Q.16 Match the column :

**Column I**

- (A) Sucrose  
(B) Maltose  
(C) Lactose  
(D) Cellulose

**Column II**

- (P) Two acetals  
(Q) No hemiacetal  
(R)  $\beta$ -1,4'-glycosidic bond  
(S) One of the hydrolysis product is glucose

Q.17 Match the column

**Column I**

**(Component of mixture)**

- (A) Crystalline  $\text{Na}_2\text{CO}_3$  + Sodium citrate +  $\text{CuSO}_4$ (aq. sol.)  
(B)  $\text{CuSO}_4$  + Rochelle Salt +  $\text{NaOH}$ (Aq. sol.)  
(C) 10%  $\alpha$  - naphthol in alcohol  
(D)  $\text{HgCl}$  +  $\text{KI}$  +  $\text{KOH}$  (aq. sol.)

**Column II**

**(Reagent)**

- (P) Fehling solution  
(Q) Nessler's Reagent  
(R) Benndict's solution  
(S) Molisch's Reagent



## EXERCISE # III

Assertion Reason

Q.1 **Statement 1** : Furanose ring, like pyranose rings are not planar.

**Statement 2** : The most stable conformation of furanose is envelope form.

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

Q.2 **Statement 1** : Bromine water changes glucose to gluconic acid.

**Statement 2** : Bromine water acts as oxidising agent.

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

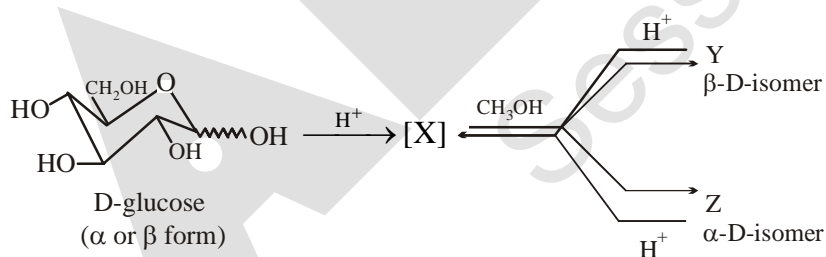
Q.3 **Statement 1** : All monosaccharide ketoses are reducing sugars.

**Statement 2** : Monosaccharide ketose give positive Tollen's and Fehling's test.

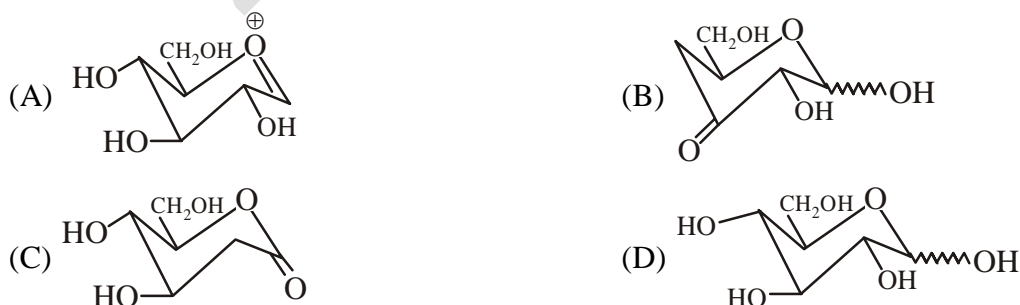
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 (C) Statement-1 is true, statement-2 is false.  
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**Comprehension (Q.4 to Q.6)**

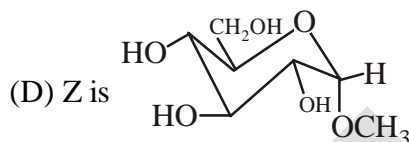
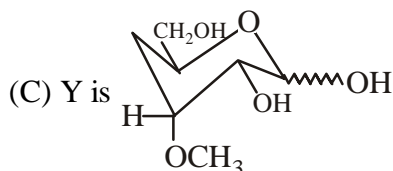
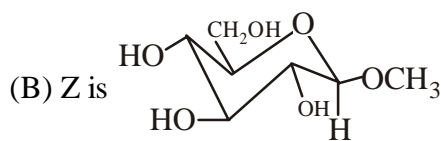
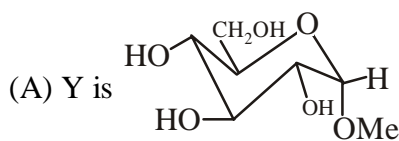
Consider the following reversible process for a reaction of D-glucose.



Q.4 The structure of intermediate [X] is



Q.5 Select the correct option.

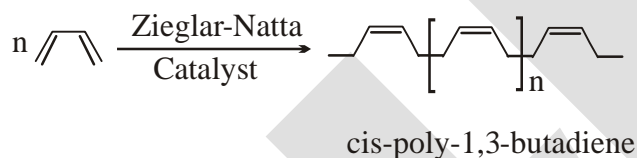


Q.6 Select the correct statement.

- (A) Y is more stable than Z due to H-bond (B) Y is less stable than Z due to anomeric effect.  
(C) Y is more stable than Z due to anomeric effect (D) Y is less stable than Z due to H-bond.

Comprehension (Q.7 to Q.9)

The monomer (G = Me or Cl) when treated with Ziegler - Natta catalyst undergo polymerisation in the manner given below -



Q.7 The Ziegler-Natta catalyst is

- (A)  $\text{TiCl}_4$  (B)  $\text{R}_3\text{Al}$  (C)  $\text{R}_3\text{Al} / \text{TiCl}_4$  (D)  $\text{R}_3\text{B} / \text{TiCl}_4$

Q.8 The polymer obtained when monomeric unit used is

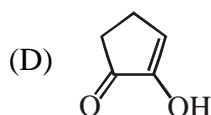
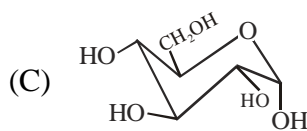
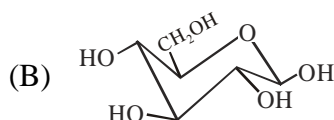
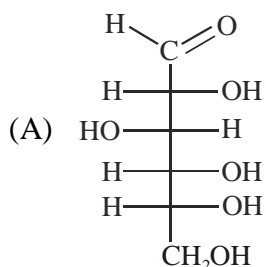
- (A) Neoprene (B) Stilbene (C) Styrene (D) Chloropren

Q.9 Which of the following statement is not true considering the process given above.

- (A) The general class of polymer formed is known as homopolymer  
(B) The polymer obtained is stereoregular  
(C) Buna-N can be prepared using above process  
(D) Synthetic rubber can be formed by above process using 1,3- butadiene.

Match the Column

Q.10 Match the compounds given below existing in equilibrium mixture with their percentage given in the right hand side.

**Column I****Column II**

(P) 36 %

(Q) 63.8 %

(R) 99.9 %

(S) 0.2 %

Q.11 Match the column :

**Column I****(Carbohydrate)**

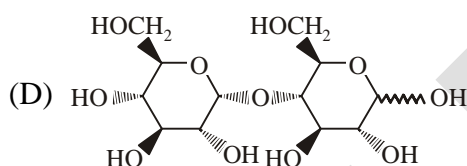
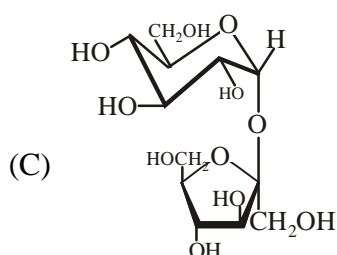
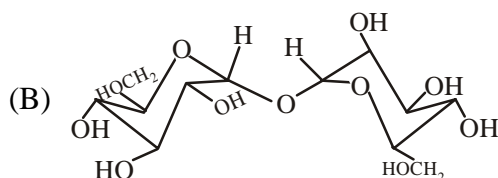
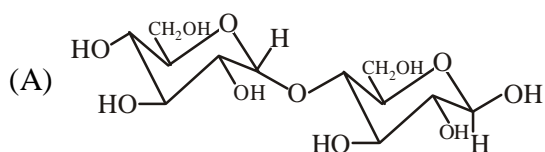
- (A) Starch  
(B) Sucrose  
(C) Lactose  
(D) Maltose

**Column II****(Properties)**

- (P) Mutarotation  
(Q) Non reducing sugar  
(R)  $\beta$ -glycosidic bond  
(S)  $\alpha$ -glycosidic bond  
(T) Reducing sugar  
(U) Hemiacetal

Q.12 Match the column :

**Column I**



**Column II**

(P)  $\alpha$ -glycoside bonds

(Q) Reducing sugar

(R) Forms enediol intermediate

(S)  $\beta$ -glycoside bond

Q.13 Match the column

**Column I**

(Functional group)

(A) Aldehydic

(B) Phenolic

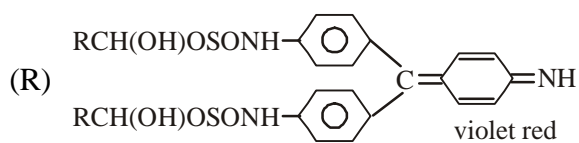
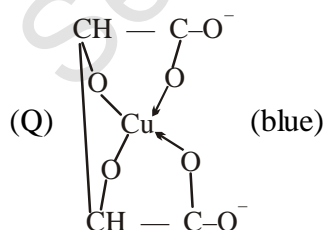
(C) Alcohol

(D)  $\alpha$ -D- Glucopyranose

**Column II**

(Test used or complex formed during confirmatory test)

(P)  $[(C_6H_5O)_6Fe]^{-3}$  (violet)



(S)  $(ROH)_2Ce(NO_3)_4$  (Red)

(T) Molisch's Test

Q.14 Match the column :

**Column I**

- (A) Addition polymer  
(B) Condensation polymer  
(C) Homopolymer  
(D) Copolymers

**Column II**

- (P) Buna-S  
(Q) Buna-N  
(R) Polythene  
(S) Nylon 6,6

Q.15 Match the column

**Presence of the element in****Na - extract**

- (A) N  
(B) S  
(C) N and S together

**Complex formed in one of the test**

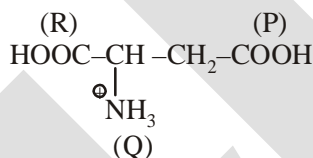
- (P)  $\text{Na}_4[\text{Fe}(\text{CN})_5\text{NOS}]$   
(Q)  $\text{Fe}(\text{CNS})_3$   
(R) PbS  
(S)  $\text{Fe}_4[\text{Fe}(\text{CN})_6]$

**Colour of the complex**

- (W) Prussian Blue  
(X) Black  
(Y) Violet  
(Z) Blood Red

**Subjective Type :**

Q.16 The pKa values for the three acidic group P,Q,R are 4.3, 9.7 and 2.2 respectively



Calculate the isoelectric point of the amino acid ?

Q.17 How will you separate?

- |                                                     |                                              |
|-----------------------------------------------------|----------------------------------------------|
| (a) Ethane & Ethyne                                 | (b) 1-Butyne & 2-Butyne                      |
| (c) Phenol & Propanol                               | (d) 2-Propanol & Propanone                   |
| (e) $\text{CH}_3\text{COOH}$ & $\text{HCOOCH}_3$    | (f) $\text{PhOH}$ & $\text{PhCOOH}$          |
| (g) $\text{C}_2\text{H}_4$ & $\text{C}_2\text{H}_2$ | (h) $\text{EtNH}_2$ & $\text{Me}_2\text{NH}$ |
| (i) $\text{EtOH}$ & $\text{Et}-\text{O}-\text{Et}$  |                                              |

Q.18 How will you differentiate?

- |                                      |                                             |
|--------------------------------------|---------------------------------------------|
| (a) Propane & Propene                | (b) 1,1-Dichloroethane & 1,2-Dichloroethane |
| (c) Chloroethane & Chloroethene      | (d) Pure & Oxidized $\text{CHCl}_3$         |
| (e) p-chlorotoluene & benzylchloride | (f) n-propylchloride & isopropylchloride    |
| (g) Methanol & ethanol               | (h) Isobutanol & tert-butanol               |

(i) 2-Pentanol & 3-pentanol

(k) Ethanol & Propanol

(m) HCHO & PhCHO

(o) HCOOH & CH<sub>3</sub>COOH

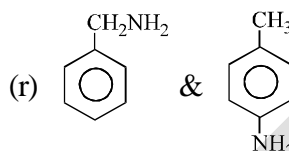
(q) MeNH<sub>2</sub> & Me<sub>2</sub>NH

(j) O-cresol & benzylalcohol

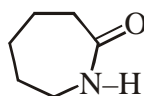
(l) Propanone & Ethanol

(n) Glucose & Fructose

(p) HCOOH & HCHO



Q.19 (a) What is the structure of nylon-6, made by alkaline polymerisation of caprolactam.



(b) Suggest mechanism for the process. Is polymerisation of the chain reaction or step reaction type.

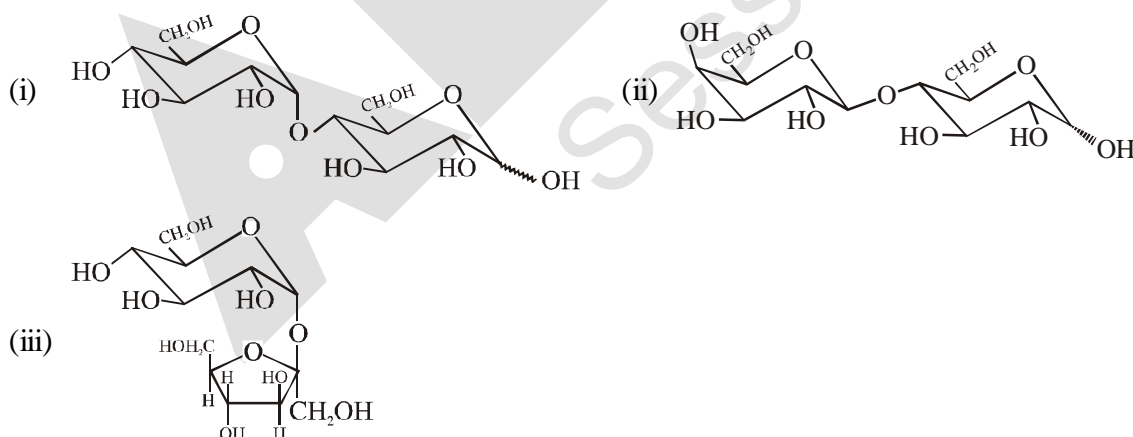
Q.20 Compound (A) C<sub>5</sub>H<sub>10</sub>O<sub>5</sub> give a tetra-acetate with Ac<sub>2</sub>O & oxidation of A with Br<sub>2</sub>/H<sub>2</sub>O gives an acid C<sub>5</sub>H<sub>10</sub>O<sub>6</sub>. Reduction of A with HI & Red P. Give 2-methyl butane. What is structure of 'A'?

Q.21 (i) Sulphanilic acid although has acidic as well as basic group. It is soluble in alkali but insoluble in mineral acid. Explain.

(ii) Explain why sulphonic acid is not soluble in organic solvents.

Q.22 Account for the fact that 2-amino ethanoic acid (glucine) exist as a dipolar ion as does p-aminobenzene sulphonic acid but p-amino benzoic acid does not.

Q.23 For given compound



(a) Which glycosidic linkage is present

(b) Name of the compound

(c) Products obtained on hydrolysis

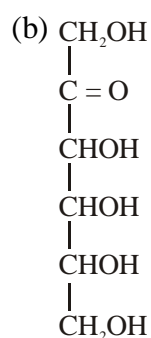
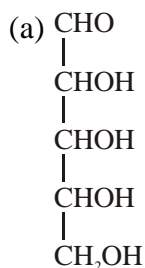
(d) Is it reducing sugar

(e) Number of moles of HIO<sub>4</sub> consumed

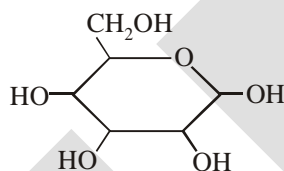
(f) Is mutarotation possible

(g) Number of moles of CH<sub>3</sub>COCl consumed per mole of compound.

Q.24 For given compound



- (i) Number of possible isomers  
 (ii) Number of possible D-configuration isomers  
 (iii) Number of possible L-configuration isomers

Q.25 Number of possible isomers of  $\alpha$ -D-glucopyranose configuration.

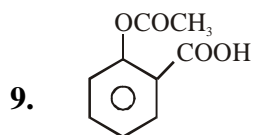
Q.26 Calculate isoelectric point of following amino acid

|                                                                                                                                                                 | pKa <sub>1</sub><br>( $\alpha$ -COOH) | pKa <sub>2</sub><br>( $\alpha$ -COOH) | pKa<br>(side chain) |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------|---------------------------------------|---------------------|
| (a) Glycine $\text{NH}_3^+ - \text{CH}_2 - \text{COOH}$                                                                                                         | 2.3                                   | 9.6                                   | —                   |
| (b) Serine $\begin{array}{c} \text{CH}_2 - \text{CH} - \text{COOH} \\   \quad   \\ \text{OH} \quad \text{NH}_3^+ \end{array}$                                   | 2.2                                   | 9.2                                   | —                   |
| (c) Alanine $\begin{array}{c} \text{NH}_3^+ \\   \\ \text{CH}_3 - \text{CH} - \text{COOH} \end{array}$                                                          | 2.3                                   | 9.7                                   | —                   |
| (d) Aspartic acid $\begin{array}{c} \text{HOOC} - \text{CH}_2 - \text{CH} - \text{COOH} \\   \\ \text{NH}_3^+ \end{array}$                                      | 2.1                                   | 9.8                                   | 3.9                 |
| (e) Lysine $\begin{array}{c} \text{NH}_3^+ - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH} - \text{COOH} \\   \\ \text{NH}_3^+ \end{array}$ | 2.2                                   | 9.0                                   | 10.5                |

EXERCISE # IV (J-MAIN)

1. Which of the following pairs give positive Tollen's test? [J-Main-2004]  
 (1) Glucose, sucrose (2) Glucose, fructose  
 (3) Hexanal, Acetophenone (4) Fructose, sucrose
2. Two forms of D – glucopyranose, are called. [J-Main-2005]  
 (1) Enantiomers (2) Anomers (3) Epimers (4) Diastereomers
3. When benzene sulfonic acid and p-nitrophenol are treated with  $\text{NaHCO}_3$ , the gases released respectively are [J-Main-2006]  
 (1)  $\text{SO}_2$ ,  $\text{NO}_2$  (2)  $\text{SO}_2$ , NO (3)  $\text{SO}_2$ ,  $\text{CO}_2$  (4)  $\text{CO}_2$ ,  $\text{CO}_2$
4. **Statement-1** : Glucose gives a reddish-brown precipitate with Fehling's solution.  
*because* [J-Main-2007]  
**Statement-2** : Reaction of glucose with Fehling's solution gives CuO and gluconic acid.  
 (1) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.  
 (2) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.  
 (3) Statement-1 is True, Statement-2 is False.  
 (4) Statement-1 is False, Statement-2 is True.
5. Which one of the following bases is **not present** in DNA ? [J-Main-2014]  
 (1) Cytosine (2) Thymine (3) Quinoline (4) Adenine
6. Which one is classified as a condensation polymer? [J-Main- 2014]  
 (1) Teflon (2) Acrylonitrile (3) Dacron (4) Neoprene
7. Which of the vitamins given below is water soluble? [J-Main- 2015]  
 (1) Vitamin E (2) Vitamin K (3) Vitamin C (4) Vitamin D
8. Which of the following compounds is not an antacid? [J-Main- 2015]  
 (1) Phenelzine (2) Ranitidine  
 (3) Aluminium hydroxide (4) Cimetidine





is used as :

[J-Main-2015]

- (1) Insecticide                      (2) Antacid                      (3) Antihistamine                      (4) Analgesic

10. Thiol group is present in :

[J-Main-2016]

- (1) Methionine                      (2) Cytosine                      (3) Cystine                      (4) Cysteine

11. The distillation technique most suited for separating glycerol from spent-lye in the soap industry is

[J-Main-2016]

- (1) Distillation under reduced pressure                      (2) Simple distillation  
(3) Fractional distillation                      (4) Steam distillation

12. Which of the following statements about low density polythene is FALSE ? [J-Main-2016]

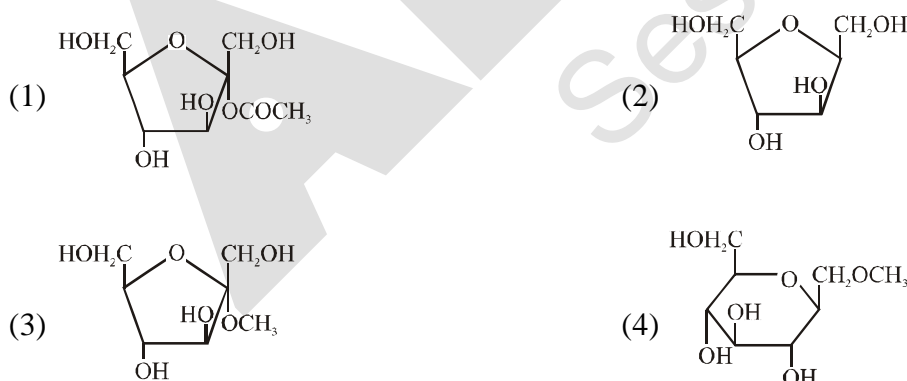
- (1) It is used in the manufacture of buckets, dust-bins etc  
(2) Its synthesis requires high pressure  
(3) It is a poor conductor of electricity  
(4) Its synthesis requires dioxygen or a peroxide initiator as a catalyst.

13. Which of the following is an anionic detergent ?

[J-Main-2016]

- (1) Glyceryl oleate                      (2) Sodium stearate  
(3) Sodium lauryl sulphate                      (4) Cetyltrimethyl ammonium bromide

14. Which of the following compounds will behave as a reducing sugar in an aqueous KOH solution



[J-Main-2017]

15. The formation of which of the following polymers involves hydrolysis reaction ? [J-Main-2017]

- (1) Nylon 6                      (2) Bakelite                      (3) Nylon 6, 6                      (4) Terylene

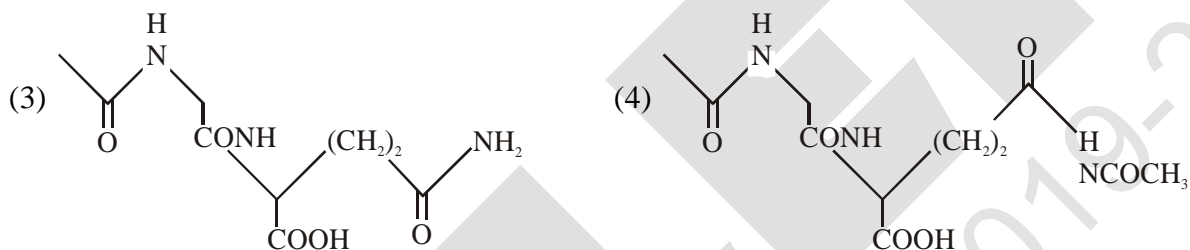
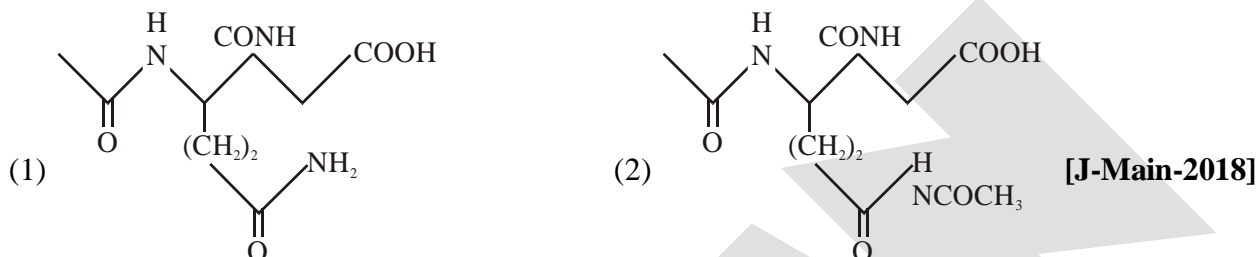
16. Glucose on prolonged heating with HI gives : [J-Main-2018]

- (1) 1-Hexene (2) Hexanoic acid (3) 6-iodohexanal (4) n-Hexane

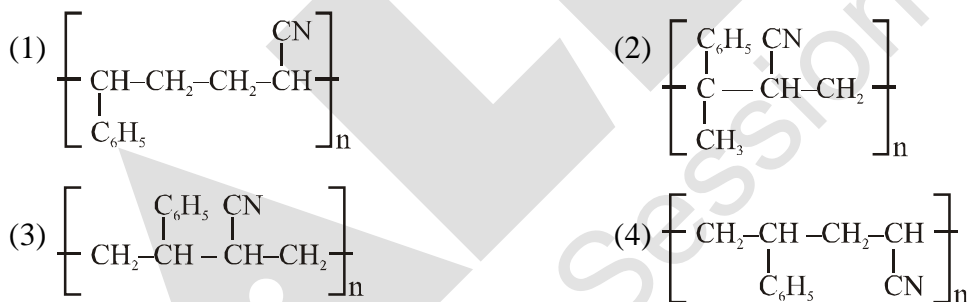
17. Which of the following statement is not true :- [J-Main-2018]

- (1) Nylon 6 is an example of step-growth polymerisation  
 (2) Chain growth polymerisation involves homopolymerisation only  
 (3) Step growth polymerisation requires a bifunctional monomer  
 (4) Chain growth polymerisation includes both homopolymerisation and copolymerisation

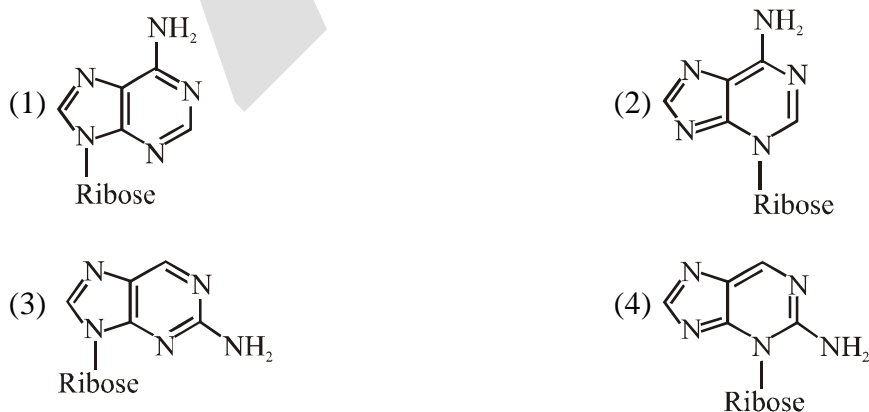
18. The dipeptide, Gln-Gly, on treatment with  $\text{CH}_3\text{COCl}$  followed by aqueous work up gives :-



19. The copolymer formed by addition polymerization of styrene and acrylonitrile in the presence of peroxide is : [J-Main-2018]



20. Which of the following is the correct structure of Adenosine ? [J-Main-2018]



21. Among the following, the incorrect statement is:-

[J-Main-2018]

- (1) Cellulose and amylose has 1, 4-glycosidic linkage.
- (2) Lactose contains  $\beta$ -D-galactose and  $\beta$ -D-glucose.
- (3) Maltose and lactose has 1, 4-glycosidic linkage.
- (4) Sucrose and amylose has 1, 2-glycosidic linkage.

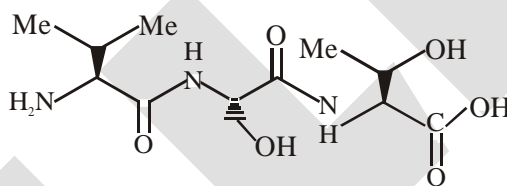
22. The correct match between items of List-I and List-II is :-

[J-Main-2018]

|     | List-I        |     | List-II    |
|-----|---------------|-----|------------|
| (A) | Phenelzine    | (P) | Pyrimidine |
| (B) | Chloroxylenol | (Q) | Furan      |
| (C) | Uracil        | (R) | Hydrazine  |
| (D) | Ranitidine    | (S) | Phenol     |

- (1) (A)-(S), (B)-(R), (C)-(P), (D)-(Q)
- (2) (A)-(R), (B)-(S), (C)-(P), (D)-(Q)
- (3) (A)-(S), (B)-(R), (C)-(Q), (D)-(P)
- (4) (A)-(R), (B)-(S), (C)-(Q), (D)-(P)

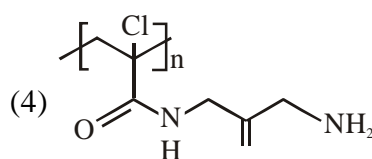
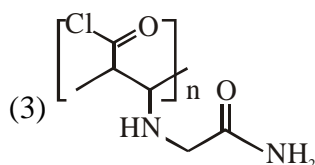
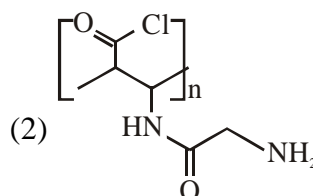
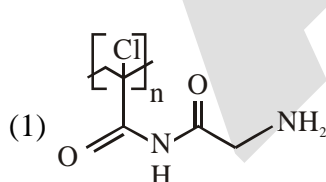
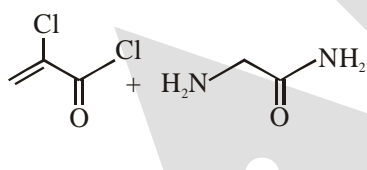
23. The correct sequence of amino acids present in the tripeptide given below is : [J-Main-(Jan)-2019]



- (1) Leu - Ser - Thr
- (2) Thr - Ser - Leu
- (3) Thr - Ser - Val
- (4) Val - Ser - Thr

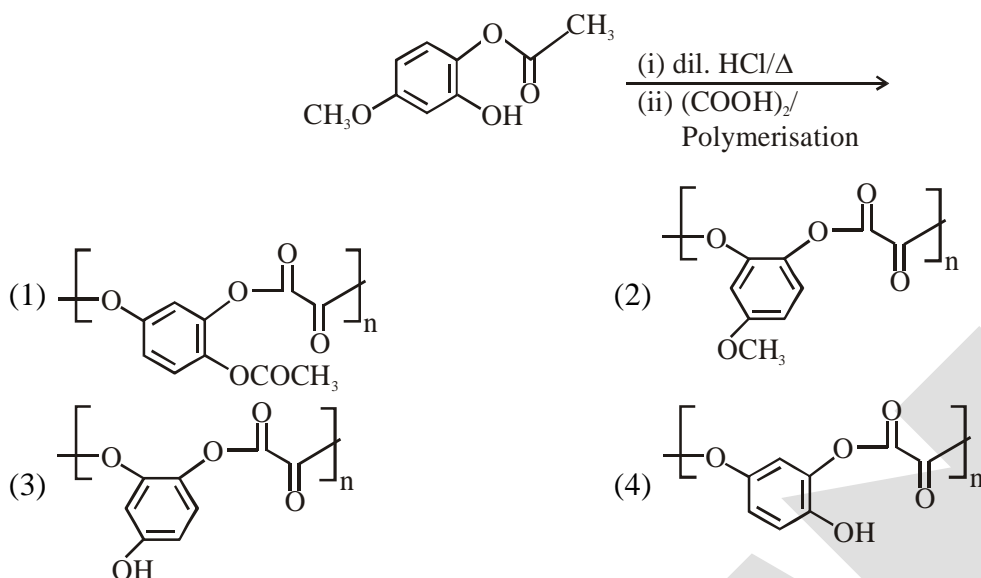
24. Major product of the following reaction is :

[J-Main-(Jan)-2019]



25. The major product of the following reaction is:

[J-Main-(Jan)-2019]



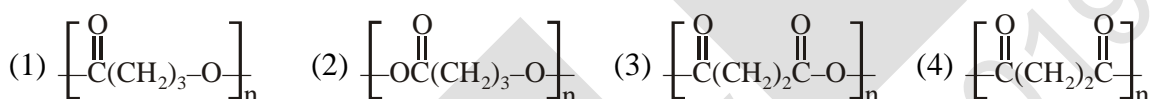
26. Which of the following tests cannot be used for identifying amino acids ?

[J-Main-(Jan)-2019]

- (1) Biuret test      (2) Xanthoproteic test      (3) Barfoed test      (4) Ninhydrin test

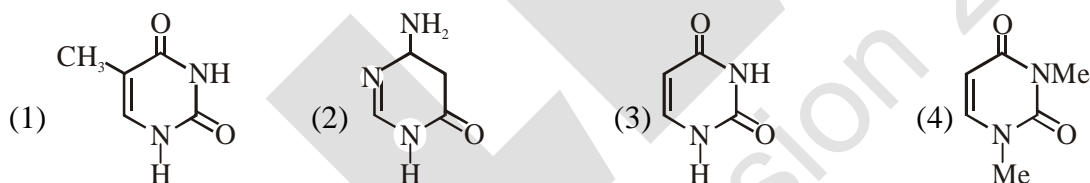
27. The homopolymer formed from 4-hydroxy-butanoic acid is :-

[J-Main-(Jan)-2019]



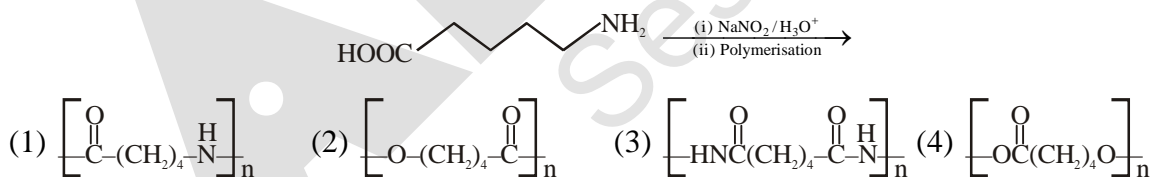
28. Among the following compound which one is found in RNA ?

[J-Main-(Jan)-2019]



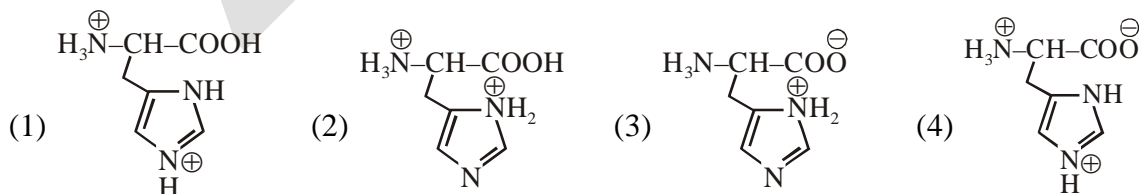
29. The polymer obtained from the following reactions is :

[J-Main-(Jan)-2019]



30. The correct structure of histidine in a strongly acidic solution (pH=2) is

[J-Main-(Jan)-2019]



31. The two monomers for the synthesis of Nylon 6, 6 are :

[J-Main-(Jan)-2019]

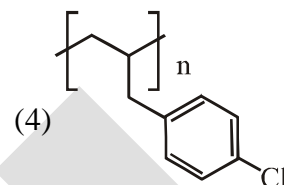
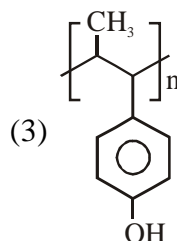
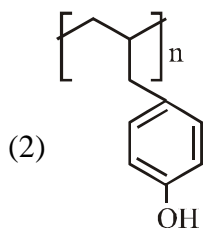
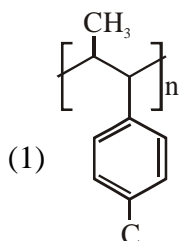
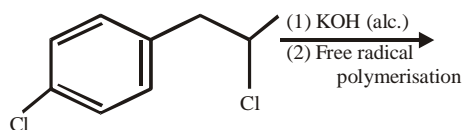
- (1)  $\text{HOOC(CH}_2)_6\text{COOH}$ ,  $\text{H}_2\text{N(CH}_2)_6\text{NH}_2$       (2)  $\text{HOOC(CH}_2)_4\text{COOH}$ ,  $\text{H}_2\text{N(CH}_2)_4\text{NH}_2$   
 (3)  $\text{HOOC(CH}_2)_6\text{COOH}$ ,  $\text{H}_2\text{N(CH}_2)_4\text{NH}_2$       (4)  $\text{HOOC(CH}_2)_4\text{COOH}$ ,  $\text{H}_2\text{N(CH}_2)_6\text{NH}_2$

32. Maltose on treatment with dilute HCl gives : [J-Main-(April)-2019]  
 (1) D-Galactose (2) D-Glucose  
 (3) D-Glucose and D-Fructose (4) D-Fructose
33. Fructose and glucose can be distinguished by : [J-Main-(April)-2019]  
 (1) Fehling's test (2) Barfoed's test  
 (3) Benedict's test (4) Seliwanoff's test
34. The peptide that gives positive ceric ammonium nitrate and carbylamine tests is : [J-Main-(April)-2019]  
 (1) Lys-Asp (2) Ser-Lys (3) Gln-Asp (4) Asp-Gln
35. Which of the following statements is not true about sucrose? [J-Main-(April)-2019]  
 (1) On hydrolysis, it produces glucose and fructose  
 (2) The glycosidic linkage is present between C<sub>1</sub> of α-glucose and C<sub>1</sub> of β-fructose  
 (3) It is also named as invert sugar  
 (4) It is a non reducing sugar
36. Number of stereo centers present in linear and cyclic structures of glucose are respectively : [J-Main-(April)-2019]  
 (1) 4 & 5 (2) 5 & 5  
 (3) 4 & 4 (4) 5 & 4
37. Amylopectin is composed of : [J-Main-(April)-2019]  
 (1) α-D-glucose, C<sub>1</sub>-C<sub>4</sub> and C<sub>1</sub>-C<sub>6</sub> linkages  
 (2) α-D-glucose, C<sub>1</sub>-C<sub>4</sub> and C<sub>2</sub>-C<sub>6</sub> linkages  
 (3) β-D-glucose, C<sub>1</sub>-C<sub>4</sub> and C<sub>2</sub>-C<sub>6</sub> linkages  
 (4) β-D-Glucose, C<sub>1</sub>-C<sub>4</sub> and C<sub>1</sub>-C<sub>6</sub> linkages
38. Which of the following statements is not true about RNA ? [J-Main-(April)-2019]  
 (1) It has always double stranded α-helix structure  
 (2) It usually does not replicate  
 (3) It is present in the nucleus of the cell  
 (4) It controls the synthesis of protein
39. Which of the following compounds is a constituent of the polymer [J-Main-(April)-2019]  

$$\left[ \text{HN} - \overset{\text{O}}{\parallel} \text{C} - \text{NH} - \text{CH}_2 \right]_n ?$$
 (1) Formaldehyde (2) Ammonia (3) Methylamine (4) N-Methyl urea

40. The major product of the following reaction is :

**[J-Main-(April)-2019]**



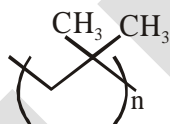
**41.** Which of the following is a condensation polymer ?

**[J-Main-(April)-2019]**

- (1) Buna - S                                          (2) Nylon 6, 6  
(3) Teflon                                            (4) Neoprene

**42.** The correct name of the following polymer is:

**[J-Main-(April)-2019]**



- |                   |                     |
|-------------------|---------------------|
| (1) Polyisoprene  | Polytert-butylene   |
| (3) Polyisobutane | (4) Polyisobutylene |

**43.** Which of the following is a thermosetting polymer?

**[J-Main-(April)-2019]**

- (1) Buna-N                  (2) PVC                  (3) Bakelite                  (4) Nylon 6

## EXERCISE # V (A) (J-ADVANCE) (OBJECTIVE)

Q.1 **Statement-1** : p-Hydroxybenzoic acid has a lower boiling point than o-hydroxybenzoic acid.

*because*

[JEE 2007]

**Statement-2** : o-Hydroxybenzoic acid has intramolecular hydrogen bonding.

(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.

(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.

(C) Statement-1 is True, Statement-2 is False.

(D) Statement-1 is False, Statement-2 is True.

Q.2 Match the chemical substances in Column I with type of polymers / type of bonds in Column II. Indicate your answer by darkening the appropriate bubbles of the  $4 \times 4$  matrix given in the ORS.

[JEE 2007]

**Column I**

- (A) Cellulose
- (B) Nylon-6, 6
- (C) Protein
- (D) Sucrose

**Column II**

- (P) Natural polymer
- (Q) Synthetic polymer
- (R) amide linkage
- (S) Glycoside linkage

Q.3 Match the compounds/ion in column I with their properties/ reaction in Column II. Indicate your answer by darkening the appropriate bubbles of the  $4 \times 4$  matrix given in the ORS.

[JEE 2007]

**Column I**

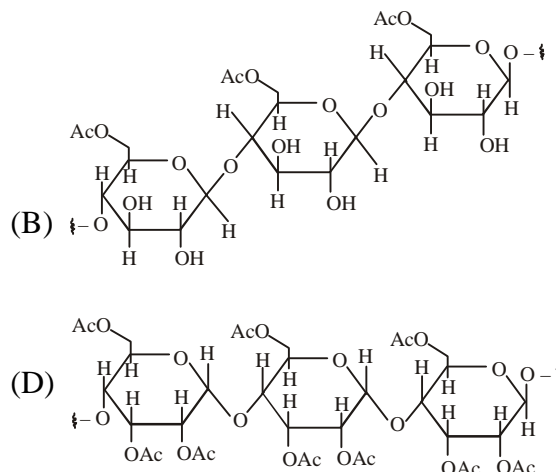
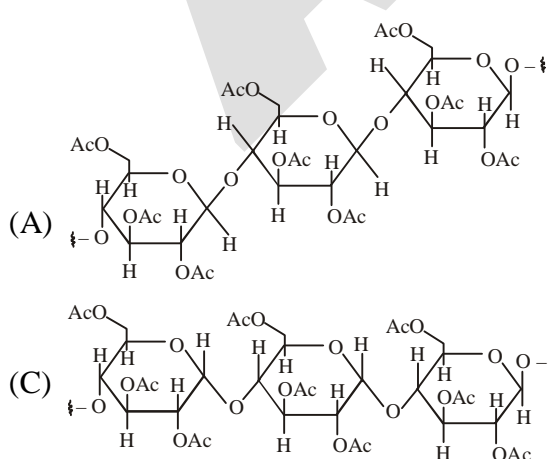
- (A)  $C_6H_5CHO$
- (B)  $CH_3C \equiv CH$
- (C)  $CN^-$
- (D)  $I^-$

**Column II**

- (P) gives precipitate with 2,4-dinitrophenylhydrazine
- (Q) gives precipitate with  $AgNO_3$
- (R) is a nucleophile
- (S) is involved in cyanohydrin formation

Q.4 Cellulose upon acetylation with excess acetic anhydride /  $H_2SO_4$  (catalytic) gives cellulose triacetate whose structure is

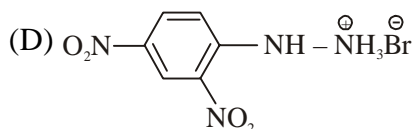
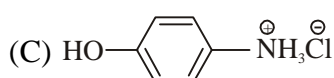
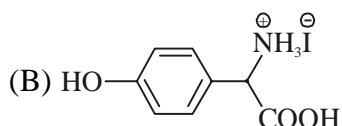
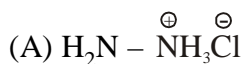
[JEE 2008]



Q.5 Match the compounds in **Column I** with their characteristic test(s)/reaction(s) given in **Column II**. Indicate your answer by darkening the appropriate bubbles of the  $4 \times 4$  matrix given in the ORS.

[JEE 2008]

**Column-I**



**Column II**

(P) Sodium fusion extract of the compound gives Prussian blue colour with  $\text{FeSO}_4$

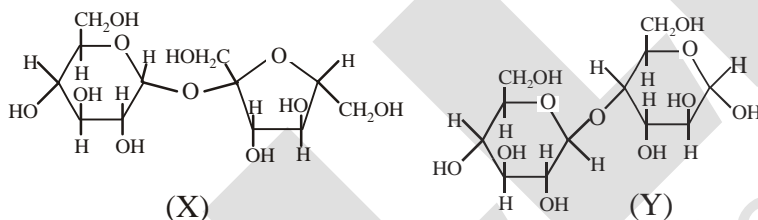
(Q) Gives positive  $\text{FeCl}_3$  test

(R) Gives white precipitate with  $\text{AgNO}_3$

(S) Reacts with aldehydes to form the corresponding Hydrazone derivative

Q.6 The correct statement(s) about the following sugars X and Y is(are)

[JEE 2009]



- (A) X is a reducing sugar and Y is a non-reducing sugar  
 (B) X is a non-reducing sugar and Y is a reducing sugar  
 (C) The glucosidic linkages in X and Y are  $\alpha$  and  $\beta$ , respectively.  
 (D) The glucosidic linkages in X and Y are  $\beta$  and  $\alpha$ , respectively

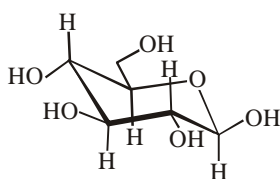
Q.7 Among cellulose, poly(vinyl chloride), nylon and natural rubber, the polymer in which the intermolecular force of attraction is weakest is

[JEE 2009]

- (A) Nylon  
 (B) Poly (vinyl chloride)  
 (C) Cellulose  
 (D) Natural Rubber

Q.8 The following carbohydrate is

[JEE 2011]

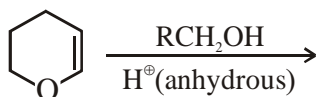


- (A) a ketohexose  
 (B) an aldohexose  
 (C) an  $\alpha$ -furanose  
 (D) an  $\alpha$ -pyranose



Q.9 The major product of the following reaction is

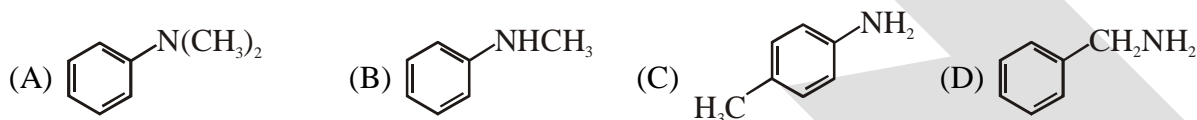
[JEE 2011]



- (A) a hemiacetal      (B) an acetal      (C) an ether      (D) an ester

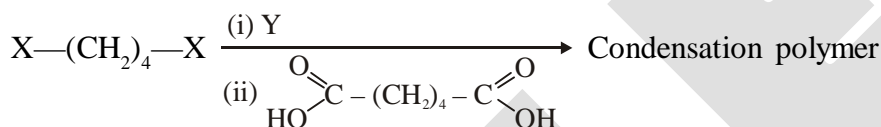
Q.10 Amongst the compounds given, the one that would form a brilliant coloured dye on treatment with  $\text{NaNO}_2$  in dil.  $\text{HCl}$  followed by addition to an alkaline solution of  $\beta$ -naphthol is -

[JEE 2011]



Q.11 The correct functional group X and the reagent/reaction conditions Y in the following scheme are

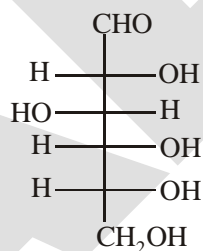
[JEE 2011]



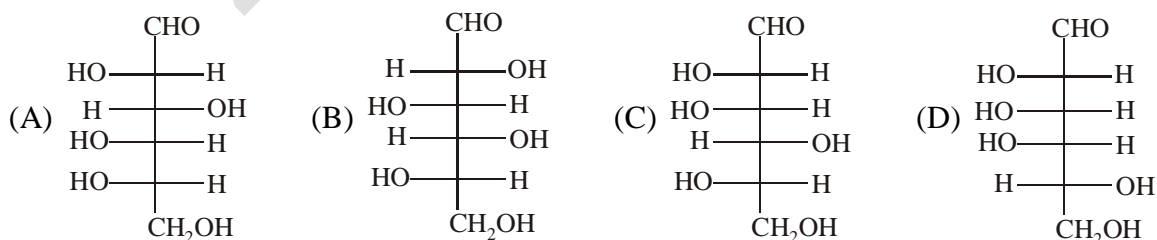
- (A)  $\text{X} = \text{COOCH}_3$ ,  $\text{Y} = \text{H}_2 / \text{Ni} / \text{heat}$       (B)  $\text{X} = \text{CONH}_2$ ,  $\text{Y} = \text{H}_2 / \text{Ni} / \text{heat}$   
 (C)  $\text{X} = \text{CONH}_2$ ,  $\text{Y} = \text{Br}_2 / \text{NaOH}$       (D)  $\text{X} = \text{CN}$ ,  $\text{Y} = \text{H}_2 / \text{Ni} / \text{heat}$

Q.12 The structure of D-(+)-glucose is

[IIT 2011]



The structure of L(-)-glucose is



Q.13 For 'invert sugar', the correct statement(s) is (are) :

[JEE 2016]

(Given : specific rotations of (+)-sucrose, (+)-maltose, L-(−)-glucose and L-(+)-fructose in aqueous solution are  $+66^\circ$ ,  $+140^\circ$ ,  $-52^\circ$  and  $+92^\circ$ , respectively)

- (A) 'invert sugar' is prepared by acid catalyzed hydrolysis of maltose
- (B) 'invert sugar' is an equimolar mixture of D-(+) glucose and D-(−)-fructose
- (C) specific rotation of 'invert sugar' is  $-20^\circ$
- (D) on reaction with  $\text{Br}_2$  water, 'invert sugar' forms saccharic acid as one of the products

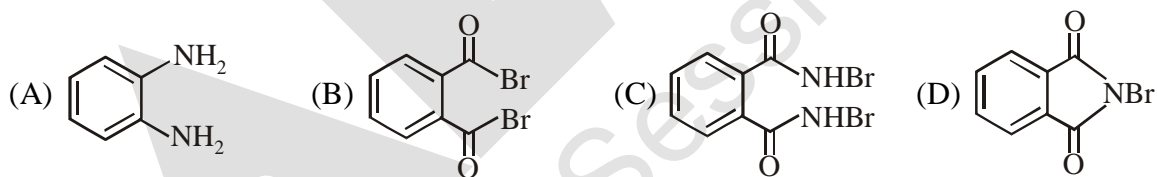
**Comprehension : Q.No. 14 to 15**

Treatment of compound **O** with  $\text{KMnO}_4 / \text{H}^+$  gave **P**, which on heating with ammonia gave **Q**. The compound **Q** on treatment with  $\text{Br}_2 / \text{NaOH}$  produced **R**. On strong heating, **Q** gave **S**, which on further treatment with ethyl 2-bromopropionate in the presence of  $\text{KOH}$  following by acidification, gave a compound **T**.



Q.14 The compound **R** is :

[JEE 2016]



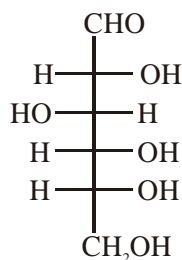
Q.15 The compound **T** is :

[JEE 2016]

- (A) Glycine
- (B) Alanine
- (C) Valine
- (D) Serine

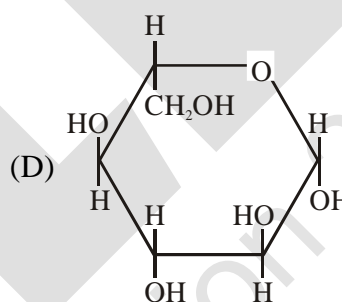
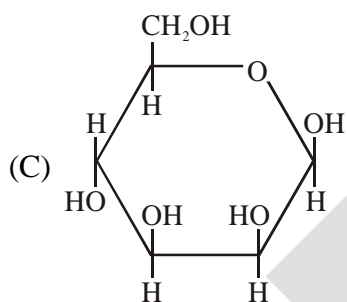
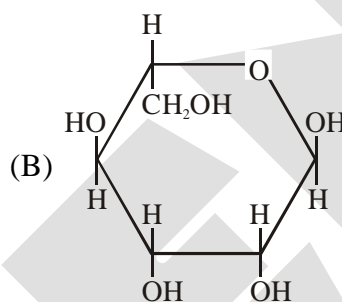
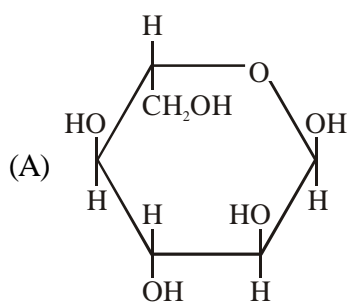
16. The Fischer presentation of D-glucose is given below.

[JEE 2018]



D-glucose

The correct structure(s) of  $\beta$ -L-glucopyranose is (are) :-



17. Which of the following statement(s) is(are) true ?

[JEE 2019]

- (A) Oxidation of glucose with bromine water gives glutamic acid
- (B) The two six-membered cyclic hemiacetal forms of D-(+)-glucose are called anomers
- (C) Hydrolysis of sucrose gives dextrorotatory glucose and laevorotatory fructose
- (D) Monosaccharides **cannot** be hydrolysed to give polyhydroxy aldehydes and ketones

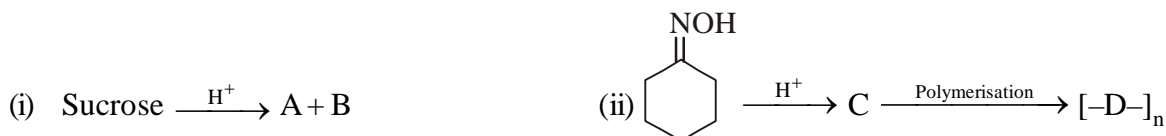
18. Choose the correct option(s) from the following

[JEE 2019]

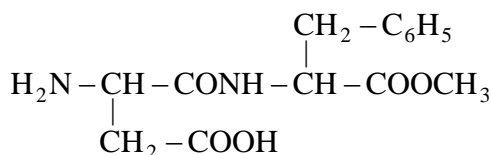
- (A) Natural rubber is polyisoprene containing *trans* alkene units
- (B) Nylon-6 has amide linkages
- (C) Cellulose has only  $\alpha$ -D-glucose units that are joined by glycosidic linkages
- (D) Teflon prepared by heating tetrafluoroethene in presence of a persulphate catalyst at high pressure

EXERCISE # V (B) (J-ADVANCE) (SUBJECTIVE)

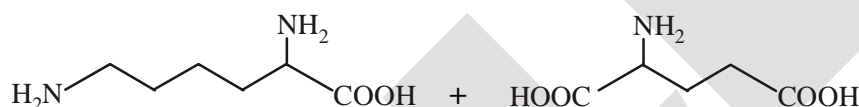
Q.1 Give the structures of the products in each of the following reactions. [JEE 2000]



Q.2 Aspartame, an artificial sweetener, is a peptide and has the following structure: [JEE 2001]

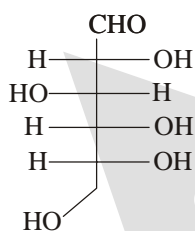


- Identify the four functional groups
  - Write the zwitterionic structure
  - Write the structures of the amino acids obtained from the hydrolysis of aspartame
  - Which of the two amino acids is more hydrophobic ?
- Q.3 Following two amino acids lysine and glutamine form dipeptide linkage. What are two possible dipeptides ? [JEE 2003]



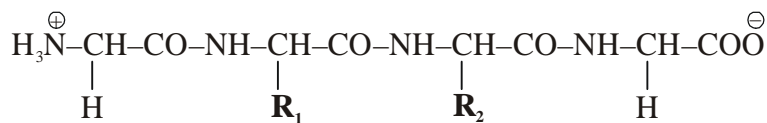
Q.4 The structure of D-Glucose is as follows- [JEE 2004]

- Draw the structure of L -Glucose
- Give the reaction of L - Glucose with Tollens reagent.



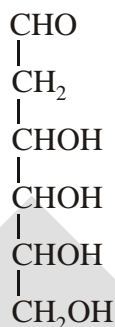
- Q.5 Monomer A of a polymer on ozonolysis yields two moles of HCHO and one mole of  $\text{CH}_3\text{COCHO}$ . [JEE 2005]
- Deduce the structure of A.
  - Write the structure of “all cis” – form of polymer of compound A.
- Q.6 A decapeptide (Mol. Wt. 796) on complete hydrolysis gives glycine (Mol. Wt. 75), alanine and phenylalanine. Glycine contributes 47.0% to the total weight of the hydrolysed products. The number of glycine units present in the decapeptide is [JEE 2011]

- Q.7 The substitutes  $R_1$  and  $R_2$  for nine peptides are listed in the table given below. How many of these peptides are positively charged at pH = 7.0 ? [JEE 2012]

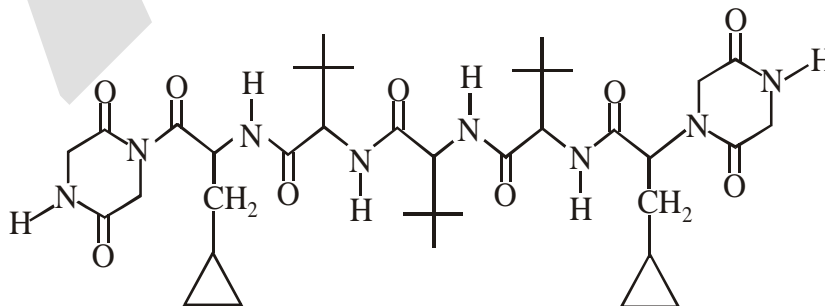


| Peptide                     | $R_1$                        | $R_2$                        |
|-----------------------------|------------------------------|------------------------------|
| I                           | H                            | H                            |
| II                          | H                            | $\text{CH}_3$                |
| III                         | $\text{CH}_2\text{COOH}$     | H                            |
| IV                          | $\text{CH}_2\text{CONH}_2$   | $(\text{CH}_2)_4\text{NH}_2$ |
| V                           | $\text{CH}_2\text{CONH}_2$   | $\text{CH}_2\text{CONH}_2$   |
| VI                          | $(\text{CH}_2)_4\text{NH}_2$ | $(\text{CH}_2)_4\text{NH}_2$ |
| VII                         | $\text{CH}_2\text{COOH}$     | $\text{CH}_2\text{CONH}_2$   |
| VIII $\text{CH}_2\text{OH}$ | $(\text{CH}_2)_4\text{NH}_2$ |                              |
| IX                          | $(\text{CH}_2)_4\text{NH}_2$ | $\text{CH}_3$                |

- Q.8 When the following aldohexose exists in its d-configuration, the total number of stereoisomers in its pyranose form is - [JEE 2012]



- Q.9. A tetrapeptide has  $-\text{COOH}$  group on alanine. This produces glycine (Gly), valine (Val), phenyl alanine (Phe) and alanine (Ala), on complete hydrolysis. For this tetrapeptide, the number of possible sequences (Primary structures) with  $-\text{NH}_2$  group attached to a chiral center is [JEE 2013]
- Q.10. The total number of lone-pairs of electrons in melamine is : [JEE 2013]
- Q.11 The total number of distinct naturally occurring amino acids obtained by complete acidic hydrolysis of the peptide shown below is : [JEE 2014]



## ANSWER-KEY

## EXERCISE # I

|                      |                      |                      |                      |                      |
|----------------------|----------------------|----------------------|----------------------|----------------------|
| <b>Q.1 Ans. (C)</b>  | <b>Q.2 Ans. (D)</b>  | <b>Q.3 Ans. (C)</b>  | <b>Q.4 Ans. (B)</b>  | <b>Q.5 Ans. (C)</b>  |
| <b>Q.6 Ans. (A)</b>  | <b>Q.7 Ans. (C)</b>  | <b>Q.8 Ans. (D)</b>  | <b>Q.9 Ans. (C)</b>  | <b>Q.10 Ans. (B)</b> |
| <b>Q.11 Ans. (B)</b> | <b>Q.12 Ans. (C)</b> | <b>Q.13 Ans. (C)</b> | <b>Q.14 Ans. (A)</b> | <b>Q.15 Ans. (A)</b> |
| <b>Q.16 Ans. (D)</b> | <b>Q.17 Ans. (D)</b> | <b>Q.18 Ans. (D)</b> | <b>Q.19 Ans. (B)</b> | <b>Q.20 Ans. (B)</b> |
| <b>Q.21 Ans. (D)</b> | <b>Q.22 Ans. (B)</b> | <b>Q.23 Ans. (A)</b> | <b>Q.24 Ans. (A)</b> | <b>Q.25 Ans. (C)</b> |
| <b>Q.26 Ans. (A)</b> | <b>Q.27 Ans. (D)</b> | <b>Q.28 Ans. (B)</b> | <b>Q.29 Ans. (B)</b> | <b>Q.30 Ans. (C)</b> |
| <b>Q.31 Ans. (C)</b> | <b>Q.32 Ans. (C)</b> | <b>Q.33 Ans. (D)</b> | <b>Q.34 Ans. (C)</b> | <b>Q.35 Ans. (A)</b> |
| <b>Q.36 Ans. (D)</b> | <b>Q.37 Ans. (B)</b> | <b>Q.38 Ans. (C)</b> | <b>Q.39 Ans. (A)</b> | <b>Q.40 Ans. (A)</b> |
| <b>Q.41 Ans. (B)</b> | <b>Q.42 Ans. (B)</b> |                      |                      |                      |

## EXERCISE # II

Q.1 Ans. (A,B,C,D) Q.2 Ans. (A,B,D) Q.3 Ans. (A,B,C) Q.4 Ans. (A,B,D) Q.5 Ans. (A,B,D)  
Q.6 Ans. (A,B,C) Q.7 Ans. (B,C) Q.8 Ans. (A,B,C,D) Q.9 Ans. (A,B,C) Q.10 Ans. (B,D)  
Q.11 Ans. (D) Q.12 Ans. (A) Q.13 Ans. (D) Q.14 Ans. (B) Q.15 Ans. (C)  
Q.16 Ans. (A)  $\rightarrow$  P, Q, S ; (B)  $\rightarrow$  S ; (C)  $\rightarrow$  R, S ; (D)  $\rightarrow$  Q, R, S  
Q.17 Ans. (A)  $\rightarrow$  R ; (B)  $\rightarrow$  P ; (C)  $\rightarrow$  S ; (D)  $\rightarrow$  Q

## EXERCISE # III

## Assertion Reason

**Q.1 Ans. (A)      Q.2 Ans. (A)      Q.3 Ans. (A)      Q.4 Ans. (A)      Q.5 Ans. (D)**  
**Q.6 Ans. (B)      Q.7 Ans. (C)      Q.8 Ans. (A)      Q.9 Ans. (C)**

### Match the Column

**Q.10 Ans. (A)  $\rightarrow$  S ; (B)  $\rightarrow$  Q ; (C)  $\rightarrow$  P ; (D)  $\rightarrow$  R**

**Q.11 Ans. (A)  $\rightarrow$  Q , S ; (B)  $\rightarrow$  Q , R, S ; (C)  $\rightarrow$  P, R, T, U (D)  $\rightarrow$  P, S, T, U**

**Q.12 Ans. (A)  $\rightarrow$  P, Q, R ; (B)  $\rightarrow$  P ; (C)  $\rightarrow$  P,S ; (D)  $\rightarrow$  P, Q, R**

**Q.13 Ans. (A)  $\rightarrow$  Q, R (B)  $\rightarrow$  P, (C)  $\rightarrow$ S; (D)  $\rightarrow$ T**

**Q.14 Ans. (A) $\rightarrow$ P, Q, R ; (B)  $\rightarrow$  S ; (C) $\rightarrow$ R ; (D)  $\rightarrow$  P, Q, S**

**Q.15 Ans. (A)  $\rightarrow$  S-W (B)  $\rightarrow$  P-Y, R-X (C)  $\rightarrow$  Q-Z**

**Subjective Type :**

**Q.16 Ans. (3.25)**

## EXERCISE # IV (J-MAIN)

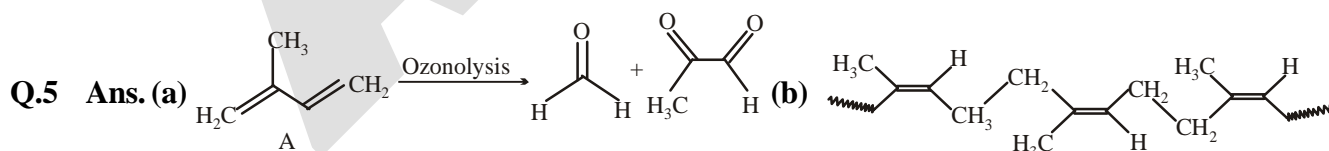
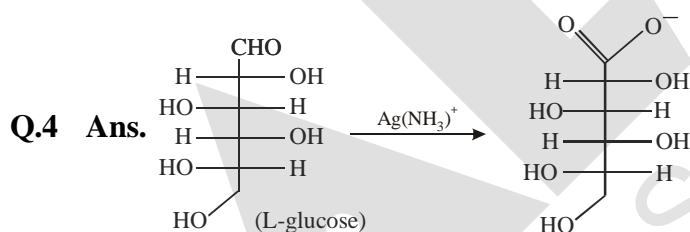
|                |                 |                 |                 |                |
|----------------|-----------------|-----------------|-----------------|----------------|
| Q.1 Ans. (2)   | Q.2 Ans. (2)    | Q.3 Ans. (4)    | Q.4 Ans.(3)     | Q.5 Ans.(3)    |
| Q.6 Ans. (3)   | Q.7 Ans. (3)    | Q.8 Ans. (1)    | Q.9 Ans.(4)     | Q.10 Ans.(4)   |
| Q.11 Ans. (1)  | Q.12 Ans. (1)   | Q.13 Ans. (3)   | Q.14 Ans.(1)    | Q.15 Ans.(1)   |
| Q.16. Ans. (4) | Q.17. Ans. (2)  | Q.18. Ans. (1)  | Q.19. Ans. (4)  | Q.20. Ans.(1)  |
| Q.21. Ans. (4) | Q.22. Ans. (2)  | Q.23. Ans. (4)  | Q. 24. Ans. (4) | Q.25. Ans.(2)  |
| Q.26. Ans.(3)  | Q.27. Ans. (1)  | Q.28. Ans. (3)  | Q. 29. Ans. (2) | Q. 30. Ans.(1) |
| Q.31. Ans.(4)  | Q. 32. Ans.(2)  | Q. 33. Ans.(4)  | Q. 34. Ans. (2) | Q. 35. Ans.(2) |
| Q.36. Ans. (1) | Q. 37. Ans.(1)  | Q. 38. Ans. (1) | Q. 39. Ans. (1) | Q. 40. Ans.(1) |
| Q.41. Ans. (2) | Q. 42. Ans. (4) | Q. 43. Ans. (3) |                 |                |

## EXERCISE # V (A) (J-ADVANCE) (OBJECTIVE)

|                                                               |                                                         |               |               |                     |
|---------------------------------------------------------------|---------------------------------------------------------|---------------|---------------|---------------------|
| Q.1 Asn. (D)                                                  | Q.2 Ans. (A) → P, S ; (B) → Q, R ; (C) → P, R ; (D) → S |               |               |                     |
| Q.3 Ans. (A) → P, S ; (B) → Q ; (C) → Q, R, S ; (D) → Q, R    |                                                         |               |               | Q.4 Ans. (A)        |
| Q.5 Ans. (A) → R, S ; (B) → P, Q ; (C) → P, Q, R ; (D) → P, S |                                                         |               |               | Q.6 Ans. (B,C)      |
| Q.7 Ans. (D)                                                  | Q.8 Ans. (B)                                            | Q.9 Ans.(B)   | Q.10 Ans. (C) | Q.11 Ans. (A,B,C,D) |
| Q.12 Ans. (A)                                                 | Q.13 Ans. (B,C)                                         | Q.14 Ans. (A) | Q.15 Ans. (B) | Q.16 Ans. (D)       |
| Q.17. Ans. (B,C,D)                                            | Q. 18 Ans. (B,D)                                        |               |               |                     |

## EXERCISE # V (B) (J-ADVANCE) (SUBJECTIVE)

Q.2 Ans. (i) Amine, carboxylic acid, Amide, Ester



|               |              |              |               |                |
|---------------|--------------|--------------|---------------|----------------|
| Q.6 Ans. (6)  | Q.7 Ans. (4) | Q.8 Ans. (8) | Q.9. Asn. (4) | Q.10. Ans. (6) |
| Q.11 Ans. (1) |              |              |               |                |

## POLYMERS AND PRACTICAL ORGANIC CHEMISTRY NOTES

- The term polymer is used to describe a very large molecule that is made up of many small repeating molecular units. These small molecular units from which the polymer is formed are called monomers.
- The chemical reaction that joins the monomers together is called polymerisation.
- Starting from  $n$  molecules of a compound  $M$ , linking in a linear manner will form polymer  $x-M-(M)_{n-2}-M-y$ . The nature of linkages at the terminal units i.e.  $M-x$  and  $M-y$  depends upon the mode of reaction used in making the polymers.

### Homopolymers and Copolymers

Polymers which are formed by only one type of monomer are called homopolymers. Some examples of homopolymers and their monomers are given below :

| Homopolymer        | Monomer              |
|--------------------|----------------------|
| Starch             | Glucose              |
| Cellulose          | Glucose              |
| Glycogen           | Glucose              |
| Dextrin            | Glucose              |
| Inulin             | Fructose             |
| Polyethylene       | Ethylene             |
| Polyvinyl chloride | Vinyl chloride       |
| Teflon             | Tetrafluoro ethylene |
| Nylon-6            | Caprolactam          |
| Polystyrene        | Styrene              |
| Orlon (Acrilan)    | Acrylonitrile        |
| Plexiglas (Lucite) | Methyl methacrylate  |
| Polyvinyl acetate  | Vinyl acetate        |

Polymers, which are formed by more than one type of monomers are known as copolymers. Some examples are given below in the table :

| Copolymer    | Monomers                               |
|--------------|----------------------------------------|
| Saran        | Vinyl chloride and vinylidene chloride |
| SAN          | Styrene and acrylonitrile              |
| ABS          | Acrylonitrile, butadiene and styrene   |
| Butyl rubber | Isobutylene and Isoprene               |
| Buna-S, SBR  | Styrene and Butadiene                  |
| Buna-N, NBR  | Acrylonitrile and Butadiene            |
| Nylon-66     | Hexamethylenediamine and Adipic acid   |
| Terylene     | Terephthalic acid and ethylene glycol  |

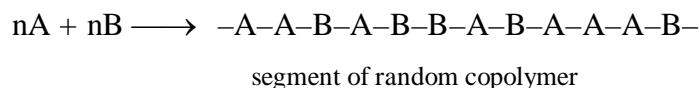


**Types of copolymers**

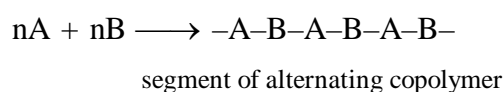
Depending upon the distribution of monomer units, the following types of copolymers are possible.

**(1) Random Copolymer**

If the monomer units have random distribution throughout the chain, it is called random copolymer. For example, if the monomer A and monomer B undergo copolymerisation then the structure of the random copolymer is

**(2) Alternating Copolymer**

If the two monomer units present alternatively throughout the polymer chain, it is said to be alternating copolymer. For example,

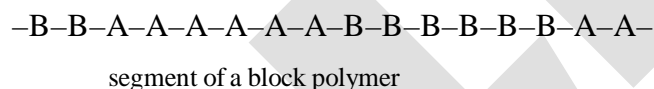


The exact distribution depends upon the proportion of the two reactant monomers and their relative reactivities. In practice neither perfectly random nor perfectly alternating copolymers are usually formed. However, most copolymers tend more towards alternating type but have many random imperfections.

**(3) Block copolymer**

Polymers in which different blocks of identical monomer units alternate with each other are called block copolymers.

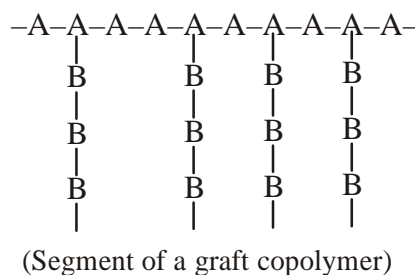
For example,



Block copolymer can be prepared by initiating the radical polymerisation of one monomer to grow homopolymer chains, followed by addition of an excess of the second monomer.

**(4) Graft copolymer**

Polymers in which homopolymer branches of one monomer unit are grafted onto a homopolymer chain of another monomer unit are called graft co-polymers. For example:



Graft copolymers are prepared by  $\gamma$ -irradiation of a homopolymer chain in the presence of a second monomer. the high energy radiation knock out H-atoms from the homopolymer chain at random points thus generating radical sites that can initiate polymerisation of the second monomer.

## CLASSIFICATION OF POLYMERS

Polymers are classified in following ways :

### (I) CLASSIFICATION BASED UPON SOURCE

#### (1) Natural polymers

Polymers which are obtained from animals and plants are known as natural polymers. Examples of natural polymers are given below.

##### Natural polymer

1. Polysaccharide
2. Proteins
3. Nucleic acid
4. Silk
5. Natural Rubber (cis polyisoprene)
6. Gutta purcha (trans polyisoprene)

##### Monomers

- Monosaccharide
- $\alpha$ -L-Amino acids
- Nucleotide
- Amino acids
- Isoprene (2-Methyl-1,3-butadiene)
- Isoprene

Natural polymers which take part in metabolic processes are known as biopolymers. Examples are polysaccharides, proteins, RNA and DNA.

#### (2) Semisynthetic polymers

Polymers which are prepared from natural polymers are known as semisynthetic polymers. Most of the semisynthetic polymers are prepared from cellulose. Examples are: cellulose acetate, cellulose nitrate, cellulose xanthate and Rayon.

#### (3) Synthetic polymers

Man-made polymers, i.e. polymers prepared in laboratory are known as synthetic polymers. Example are : PVC, polyethylene, polystyrene, nylon-6, nylon-66, nylon-610, terylene, synthetic rubbers etc.

### (II) CLASSIFICATION BASED UPON SHAPE

#### (1) Linear polymers

Polymer whose structure is linear is known as linear polymer. The various linear polymeric chains are stacked over one another to give a well packed structure.



The chains are highly ordered with respect to one another. The structure is close packed in nature, due to which they have high densities, high melting point and high tensile (pulling) strength. Linear polymers can be converted into fibres.

##### Note :

- (i) All fibers are linear polymers. Examples are cellulose, silk, nylon, terylene etc.
- (ii) Linear polymers may be condensation as well as addition polymers. Examples are cellulose, polypeptide, nucleic acid, nylon, terylene etc.

**(2) Branched chain polymers**

Branched chain polymers are those in which the monomeric units constitute a branched chain. Due to the presence of branches, these polymers do not pack well. As a result branched chain polymers have lower melting points, low densities and tensile strength as compared to linear polymers. Branched chain polymers may be formed due to addition as well as condensation polymerisation. Examples are amylopectin, glycogen, low density polyethylene.

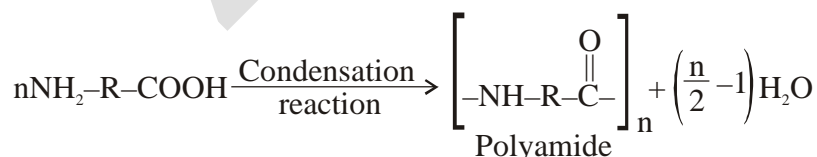
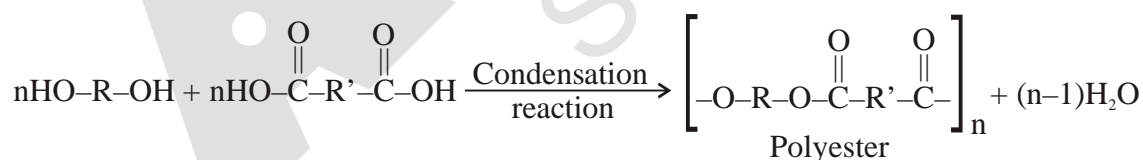
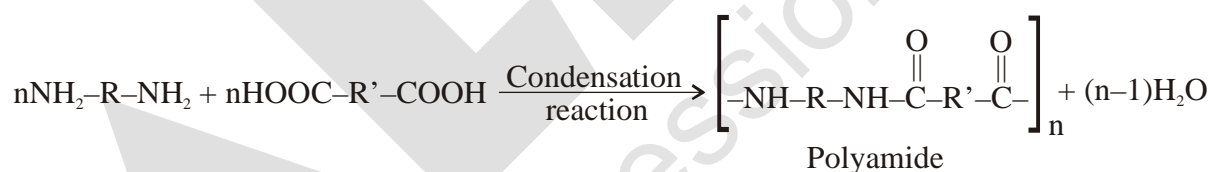
**(3) Cross-linked or Three Dimensional network polymers**

In these polymers the initially formed linear polymeric chains are joined together to form a three dimensional network structure. These polymers are hard, rigid and brittle. Cross-linked polymers are always condensation polymers. Resins are cross linked polymers, Urea-formaldehyde resin, phenol-formaldehyde resin.

**CLASSIFICATION BASED UPON SYNTHESIS****(1) Condensation polymerisation**

They are formed due to condensation reactions. Condensation polymerisation is also known as step growth polymerisation. For condensation polymerisation, monomers should have at least two functional groups. Both functional groups may be same or different. Monomers having only two functional group always give linear polymer.

For example,

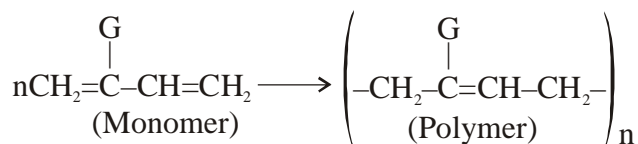


Condensation polymers do not contain all atoms initially present in the monomers. Some atoms are lost in the form of small molecules. Monomer having three functional groups always gives cross-linked polymer.

**Examples are :** Urea-formaldehyde resin, phenol-formaldehyde resin.

### (3) Addition polymerisation

Polymers which are formed by addition reaction are known as addition polymers. If monomer is ethylene or its derivative, then addition polymer is either linear polymer or branch-chain polymer. Examples are : polystyrene, polytetrafluoroethylene, polyacrylonitrile etc. If monomer is 1, 3-butadiene or 2-substituted-1, 3-butadiene  $\left( \begin{array}{c} \text{CH}_2 = \text{C} - \text{CH} = \text{CH}_2 \\ | \\ \text{G} \end{array} \right)$ , then polymer is always branched chain polymer.



#### (Monomer)

(i) G = H : 1,3 - Butadiene

(ii) G = CH<sub>3</sub> ; 2 - Methyl-1,3-butadiene or isoprene

(iii) G = Cl ; 2 -Chloro-1,3-butadiene or chloroprene

#### (Polymer)

(i) Polybutadiene

(ii) Polyisoprene

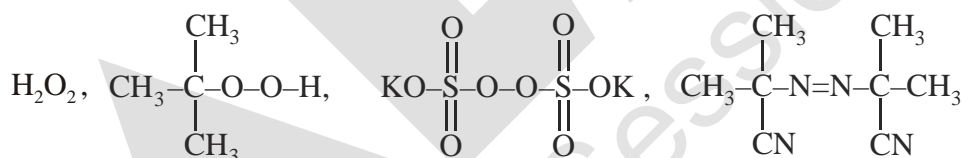
(iii) Polychloroprene (Neoprene)

Addition polymers retain all the atoms of the monomer units in the polymer. Addition polymerisation takes place in three steps. Initiation, chain propagation and chain termination. Addition polymers are called as chain growth polymers.

### Types of Addition Polymerisation

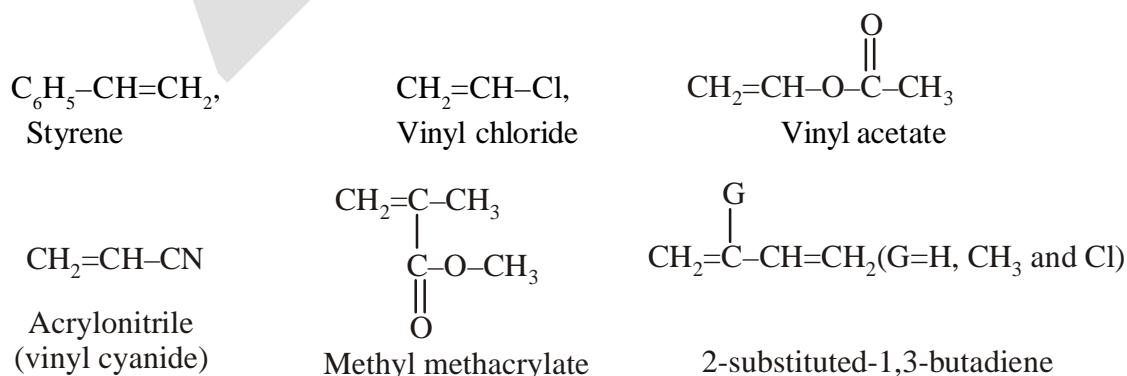
#### (A) Radical Polymerisation :

Radical polymerisation takes place in the presence of radical initiators. The radical initiator may be any of the following :



Reaction intermediate of radical polymerization is a free radical. Radical polymerization has more chance for those monomers whose free radicals are more stable.

#### Examples are :

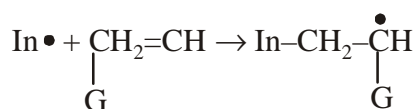
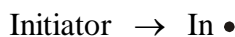


Radical polymer has linear as well as branched chain structure.

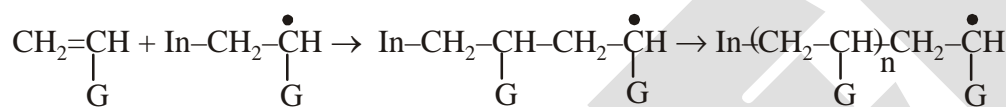
Most of the commercial addition polymers are vinyl polymers obtained from alkenes and their derivatives  $\text{CH}_2=\underset{\text{G}}{\text{CH}}$  [G is H,  $\text{C}_6\text{H}_5$ , R etc.]. This type of polymerisation is performed by heating the

monomer with only a very small amount of the initiator or by exposing the monomer to light. the general mode of radical polymerisation of vinyl monomers is depicted below :

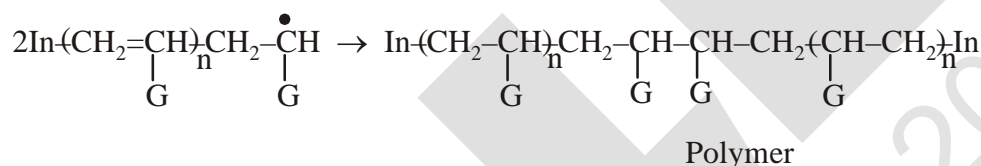
**Chain initiation step :**



**Chain propagating step :**

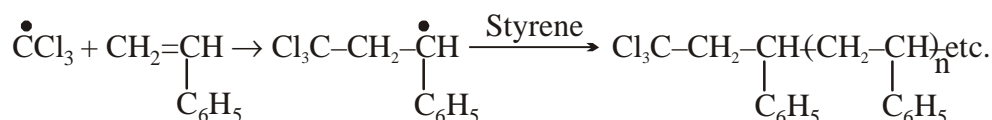
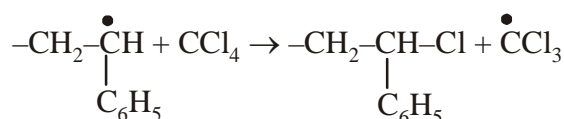


**Chain terminating step :**



In vinylic polymerisation, various other reaction of free radicals with some other compounds present may compete with the parent addition chain reactions. One such reaction takes place with molecules that can react with the growing chain to interrupt the further growth. This leads to the lowering of the average molecular mass of the polymer. Such reagents are called as chain transfer agents and include  $\text{CCl}_4$ ,  $\text{CBr}_4$  etc.

For example, in the presence of  $\text{CCl}_4$ , styrene polymerises to form polystyrene of a lower average molecular mass which also contains some chlorine what happens here is that growing polystyrene radical which normally would add on a monomer reacts with the chain transfer agent to end the original chain and produces a new radical. The latter initiates a new polymerisation chain and thereby forms a new polymer as depicted below.

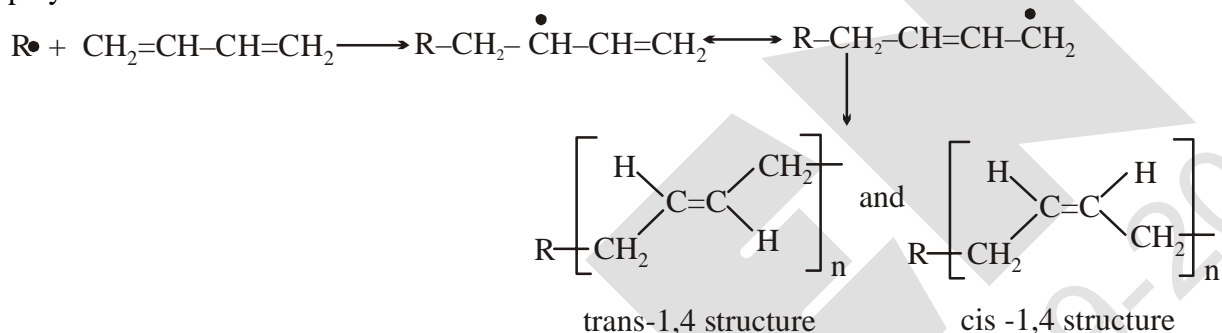


If the chain transfer agent a radical, which is highly unreactive, the reaction chain gets terminated such a compound thus inhibits or arrests polymerisation. Many amines, phenols, quinones etc. act as inhibitors. So, even traces of certain impurities, which can act as chain transfer agent or an inhibitor can interfere with the original polymerisation chain reaction. Hence, the monomers could be free from such inhibitors.

In case the alkene is a (diene), the following kinds of polymerisation is possible :

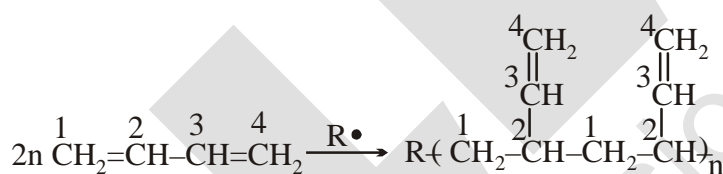
(1) **1,4 - polymerisation.**

When the polymerisation takes place at  $C_1$  and  $C_4$  of butadiene, an unbranched polymer is formed. This product is different from that formed from an alkene having a double bond, which at each of its carbons is substituted by different groups and hence can exist either as trans-polybutadiene or cis-polybutadiene or a mixture as shown below.



(2) **1,2-Polymerisation**

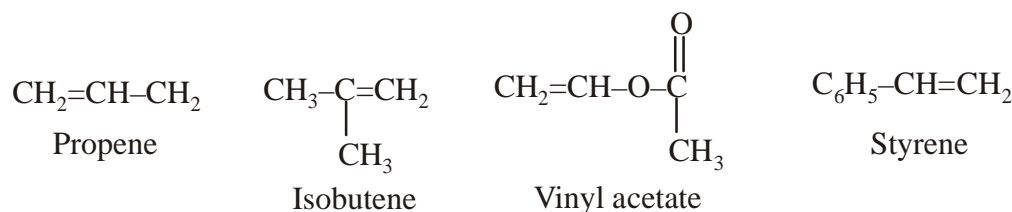
Alternatively, 1,3-butadiene can undergo polymerisation at  $C_1$  and  $C_2$  to yield the polymeric product, polyvinyl polythene.



The double bonds in these initial polymers can be linked by further treatment with chemicals to modify the properties of the polymers. These reactions form the basis of the formation of rubber.

(B) **Cationic Polymerisation :**

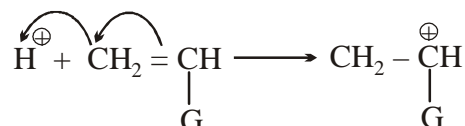
Polymerisation which is initiated by an electrophile is known as cationic polymerisation. Reaction intermediate of cationic polymerisation is a carbocation. Carbocations can undergo rearrangement leading to the formation of a more stable carbocation. The electrophile commonly used for initiation is  $BF_3 \cdot OEt_2$ . Monomers that are best able to undergo polymerisation by a cationic mechanism are those with electron - donating substituents that can stabilise the carbocation. Some examples are:



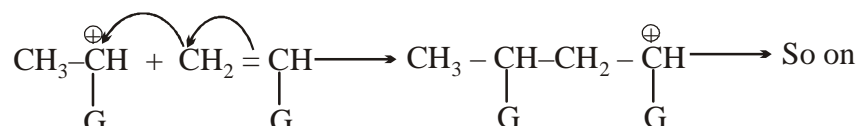
It is terminated by a base.

Thus, when the initiator is cationic in nature, it would generate a cationic intermediate on addition to the double bond for propagating the addition chain process and is termed as cationic addition polymerisation. The process is initiated by an acid. The stages of polymerisation are depicted below.

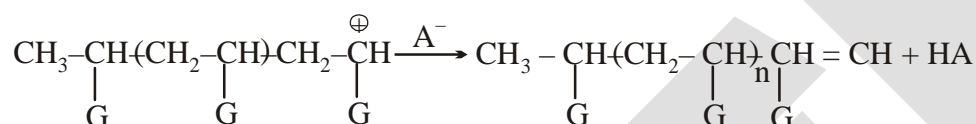
**Chain initiation step :**



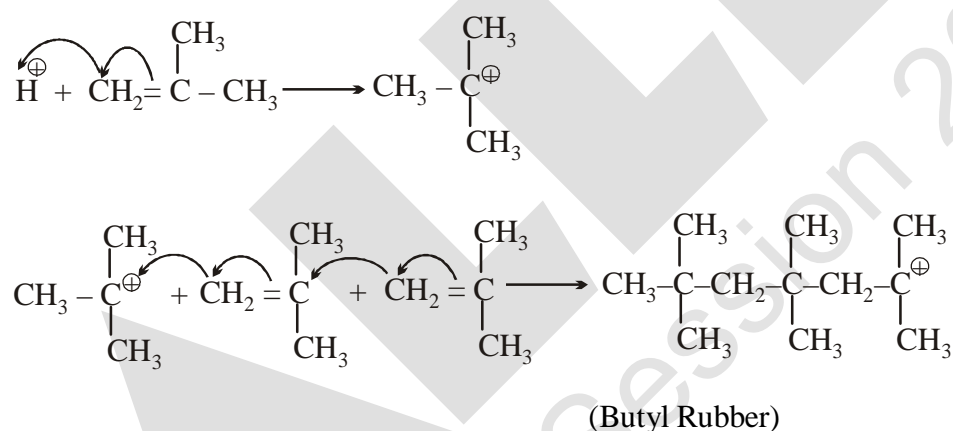
**Chain propagating step :**



**Chain terminating step :**



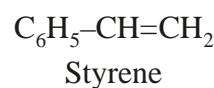
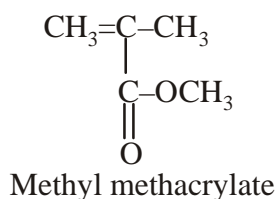
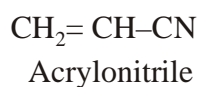
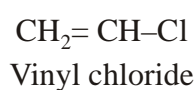
Cationic polymerisation is facilitated in monomers containing electron - releasing groups. Thus, isobutylene undergoes cationic polymerisation easily as it has two electron releasing  $-\text{CH}_3$  groups that will stabilize the intermediate carbocation.



**(C) Anionic Polymerisation :**

Anionic polymerisation takes place in the presence of base or nucleophile, which is initiator in this polymerization. Reaction intermediate in propagation steps are carboanion. The suitable initiator can be  $\text{NaNH}_2$  or  $\text{RLi}$ . Those monomers undergo anionic polymerisation reaction whose anion is stable.

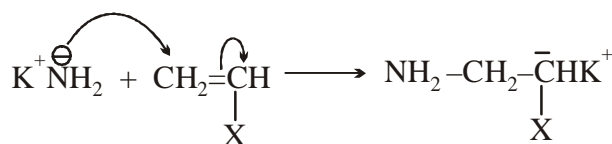
Example of monomers are :



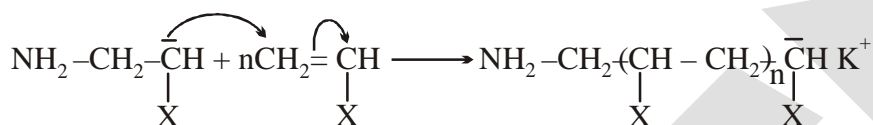
Anionic polymerisation always gives linear polymer. Anionic polymerisation terminated by an acid.

The formation of polystyrene from styrene in the presence of potassium amide is an important example of this category of polymerisation. The mode of anionic polymerisation is depicted below:

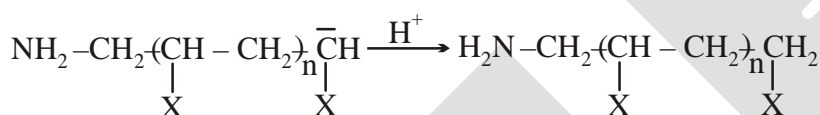
**Chain initiation step :**



**Chain propagating step :**



**Chain terminating step :**



**(D) Ziegler- Natta polymerisation :**

Addition polymerisation which takes place in the presence of Ziegler- Natta catalyst  $[(\text{C}_2\text{H}_5)_3\text{Al}$  and  $\text{TiCl}_4]$  is known as Ziegler- Natta polymerisation or coordination polymerisation. Ziegler- Natta polymerisation always gives linear, stereo-regular polymers. Ziegler- Natta catalyst revolutionised the field of polymer chemistry because they allow the synthesis of stronger and stiffer polymers (due to linear geometry) that have greater resistance to cracking and heat.

*High density polyethylene is prepared using a Ziegler- Natta catalyst.*

**CLASSIFICATION BASED ON INTERMOLECULAR FORCES**

**(SECONDARY FORCES)**

Intermolecular forces present between polymeric chains are (a) Van der waals forces (b) Hydrogen bonds and (c) Dipole - dipole attractions. Mechanical properties such as tensile strength, elasticity, toughness etc. depend upon the secondary forces present between the polymeric chains. Magnitude of secondary forces depends upon the size of the molecule and the number of functional groups along the polymeric chains. Magnitude of secondary forces is directly proportional to the length of the polymeric chain. On the basis of magnitude of secondary forces, polymers can be divided into the following categories.



**(1) Elastomes**

An elastomer is a plastic that stretches and then reverts back to its original shape. It is randomly oriented amorphous polymer. It must have some cross-links so that the chains do not slip over one another. Very weak Vander Waal forces are present in between polymeric chains.

When elastomers are stretched, the random chains stretch out, but there are insufficient Vander Waal forces to maintain them in that configuration and position. When the stretching force is removed, they go back to their random shape. Elastomers have the ability to stretch out over ten times their normal length. Important examples are vulcanized rubbers.

**Note :** Addition polymers obtained from butadiene and its derivatives are elastomers.

**(2) Fibres**

Fibres are linear polymers in which the individual chains of a polymer are held together by hydrogen bonds or dipole-dipole attraction. In the fibres, the polymeric chains are highly ordered with respect to one another. Due to strong intermolecular forces of attraction and highly ordered geometry, fibres have high tensile strength and least elasticity. They have crystalline character and have high melting points and low solubility. Examples are cellulose, nylon, terylene, wool, silk etc.

**Note :**

- (i) Condensation polymers formed from bifunctional monomers are fibres in character.
- (ii) Addition polymers of alkene derivatives having strong -I group are fibres in character.

**(3) Thermoplastic Polymers**

Thermoplastic polymers are polymers that have both ordered crystalline regions (the regions of the polymer in which the chains are highly ordered with respect to one another) and amorphous, non-crystalline regions (the regions of the polymer in which the chains are randomly oriented). The intermolecular forces of attraction are in between elastomers and fibres. There are no cross links between the polymeric chains. Thermoplastic polymers are hard at room temperature, but when they are heated, the individual chains can slip past one another and the polymer becomes soft and viscous. This soft and viscous material becomes rigid on cooling. The process of heating softening and cooling can be repeated as many times as desired without any change in chemical composition and mechanical properties of the plastic. As a result, these plastics can be moulded into toys, buckets, telephone and television cases. Some common examples are : polyethene, polypropylene, polystyrene, polyvinyl chloride, teflon etc.

**Note :** Addition polymers obtained from ethylene and ethylene derivatives are thermoplastic polymers.

**(4) Thermosetting Polymers**

Polymers which become hard on heating are called thermosetting polymers. Thermosetting polymers can be heated only once when they permanently set into a solid, which cannot be remelted by heating. Thermosetting polymers are cross-linked polymers. Greater the degree of cross-linking that exists, the more rigid is the polymer. Cross-linking reduces the mobility of the polymer chains, causing them to be relatively brittle materials. The hardening on heating is due to the extensive cross-linking between different polymer chains to give a three dimensional network solid. Examples are : phenol formaldehyde resin, urea-formaldehyde resin, melamine - formaldehyde resin.

### DIFFERENCE BETWEEN THERMOPLASTIC AND THERMOSETTING POLYMERS

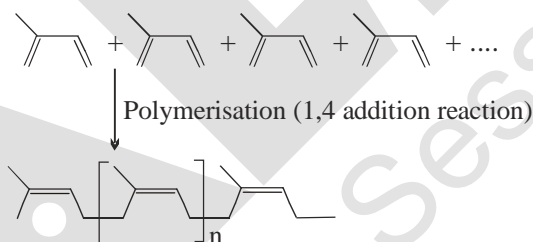
| S.No. | Thermoplastic polymers                                                           | Thermosetting polymers                                        |
|-------|----------------------------------------------------------------------------------|---------------------------------------------------------------|
| 1.    | Soften and melt on heating and become hard on cooling i.e. process is reversible | Become hard on heating and process is irreversible.           |
| 2.    | Can be moulded and remoulded and reshaped.                                       | They can be moulded once and cannot be remoulded or reshaped. |
| 3.    | They are addition polymers                                                       | They are condensation polymers.                               |
| 4.    | Structure is generally linear                                                    | Structure is cross - linked.                                  |

### RUBBER

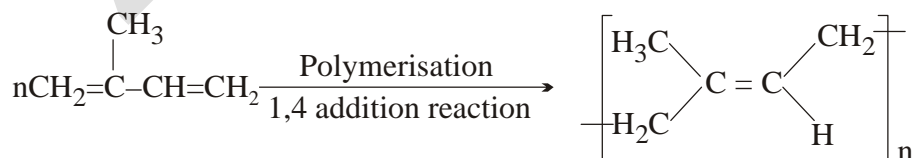
#### 1. Natural Rubber

Natural rubber is obtained from nearly five hundred different plants but the main source is a *braziliensis* tree. It is obtained in the form of milky sap known as latex. This latex is coagulated with acetic acid and formic acid. The coagulated mass is then squeezed.

The raw natural rubber is a soft gummy and sticky mass. It is insoluble in water, dilute acids and alkalies but soluble in non-polar solvents. It has low elasticity and low tensile strength. Natural rubber is a polymer of 2-methyl-1,3-butadiene (isoprene). On average, a molecule of rubber contains 5000 isoprene units held together by head to tail. All the double bonds in rubber are *cis*, hence natural rubber is *cis*-polyisoprene.

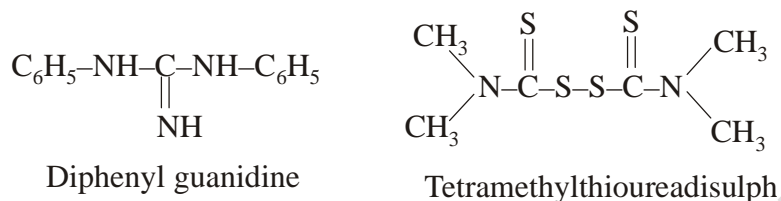


Gutta - percha is a naturally occurring isomer of rubber in which all the double bonds are *trans*. Thus, gutta-percha is *trans*-polyisoprene.



It is harder and more brittle than rubber. It is the filling material that dentists use in root canal treatment.

In order to give strength and elasticity to natural rubber, it is vulcanized. Heating of rubber with sulphur or sulphur containing compound at  $150^{\circ}\text{C}$  for few hours is known as vulcanisation. The essential feature of the vulcanisation is the formation of cross-linking between the polymeric chains. This cross-linking gives mechanical strength to the rubber. Vulcanisation process can be enhanced in the presence of certain organic compounds known as accelerators. The common accelerators are:



In addition, fillers such as carbon black and zinc oxide are usually added to the crude rubber before vulcanisation in order to improve its wearing characteristics.

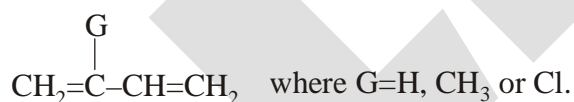
Natural rubber is used for making shoes, water - proof coats and golf balls. Vulcanised rubber is used for manufacture of rubber bands, gloves tubing and car tyres.

### SYNTHETIC RUBBER OR POLYMERISATION OF DIENES

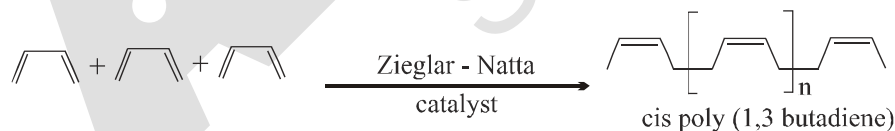
Polymers of 1,3 - butadienes are called synthetic rubbers because they have some of the properties of natural rubbers including the fact that they are water proof and elastic. Synthetic rubbers have some improved properties. They are more flexible, tougher and more durable than natural rubber.

#### 1. Homopolymers

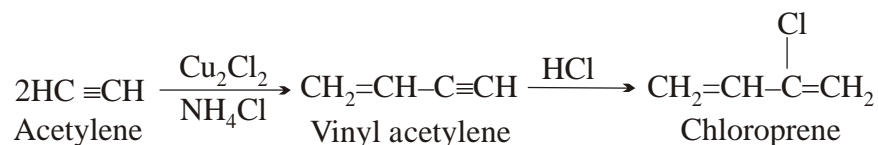
Monomer of this class is 2 - substituted - 1,3- butadienes.



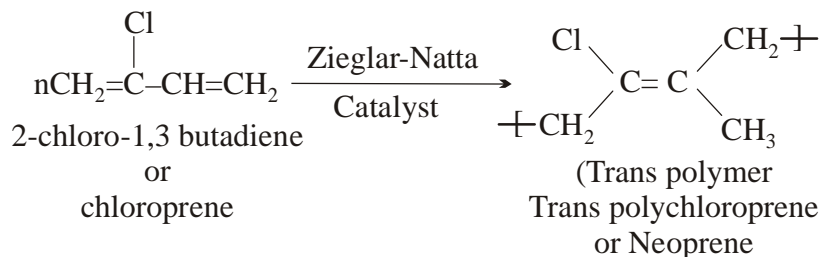
Polymerisation is always carried out in the presence of Ziegler-Natta catalyst which gives stereo regular polymers.



Neoprene was the first synthetic rubber manufactured on large scale. It is also called dieprene. Its monomer, chloroprene(2-chlorobutadiene) is prepared from acetylene.



Chloroprene undergoes free radical polymerisation to form neoprene (polychloroprene).



Many of the properties of neoprene are similar to natural rubber but neoprene is more resistant to action of oils, gasoline and other hydrocarbons. It is also resistant to sunlight, oxygen, ozone and heat. It is non - inflammable. It is used for making automobile and refrigerator parts, hoses for petrol and oil containers, insulation of electric wires and conveyor belts.

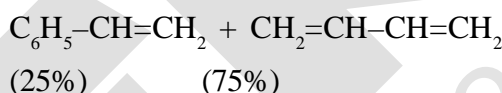
## 2. Copolymers

The following synthetic rubbers are example of copolymers.

### Synthetic rubber

1. Buna-S, SBR (Styrene-butadiene rubber)

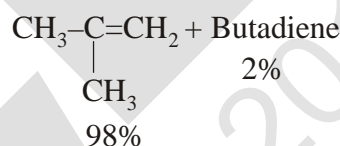
### Monomers



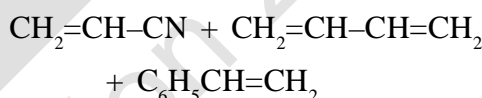
2. Buna-N, NBR (Nitrile-butadiene rubber)



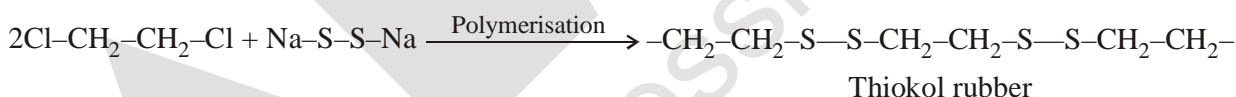
3. Butyl rubber



4. ABS; Acrylonitrile, Butadiene, Styrene

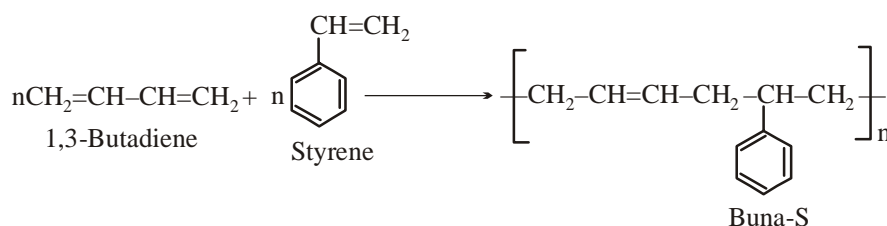


(a) **Thiokol** : Thiokol is made by polymerising ethylene chloride and sodium polysulphide.



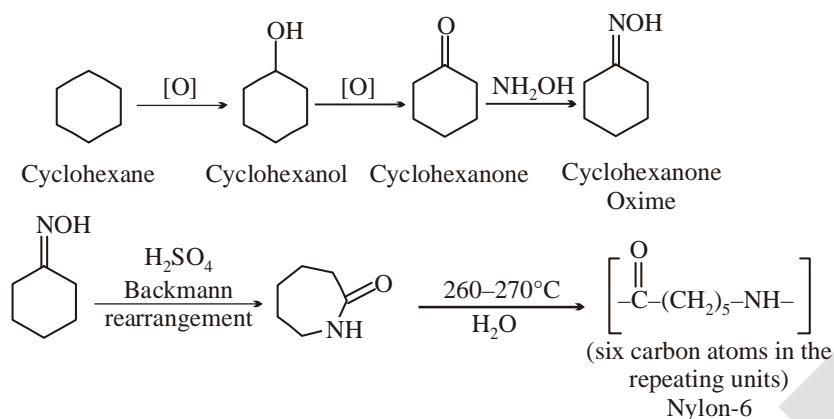
The repeating unit is  $-\text{CH}_2-\text{S}-\text{S}-\text{CH}_2-$ . Thiokol is chemically resistant polymer. It is used in the manufacture of hoses and tank linings, engine gaskets and rocket fuel when mixed with oxidising agents.

(b) **Buna -S (SBR : Styrene-butadiene rubber)** : Buna-S rubber is a copolymer of three moles of butadiene and one mole of styrene. In Buna-S, 'Bu' stands for butadiene, 'na' for symbol of sodium (Na) which is a polymerizing agent and 'S' stands for styrene. It is an elastomer (General purpose styrene Rubber or GRS).





Carpolactam is obtained by Backmann rearrangement of cyclohexanone oxime.



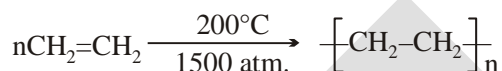
#### (4) NYON-2-NYLON-6

It is in alternating polyamide copolymer of glycine and amino caproic acid and is biodegradable.

#### POLYETHYLENE

Polyethylene is of two types :

- (a) **Low Density Poly Ethylene (LDPE)** : It is manufactured by heating ethylene at  $200^\circ C$  under a pressure of 1500 atmospheres and in the presence of traces of oxygen. This polymerisation is a free radical polymerisation.



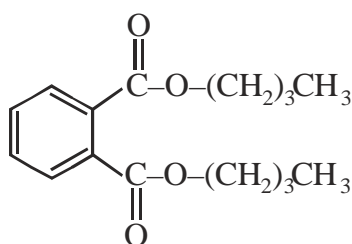
The polyethylene produced has a molecular mass of about 20,000 and has a branched structure. Due to this, polyethylene has a low density (0.92) and low melting point ( $110^\circ C$ ). That is why polyethylene prepared by free radical polymerisation is called low density polyethylene. It is a transparent polymer of moderate tensile strength and high toughness. It is widely used as a packing material and as insulation for electrical wires and cables.

- (b) **High Density Poly Ethylene (HDPE)** : It is prepared by the use of Ziegler - Natta catalyst at  $160^\circ C$  under pressure of 6 to 7 atmospheres.

The polymer is linear chain, hence it has high density (0.97) and has high melting point ( $130^\circ C$ ). That is why it is called high density polyethylene. It is a translucent polymer. It has greater toughness, hardness and tensile strength than low density polyethylene. It is used in the manufacture of containers (buckets, tubes), house wares, bottles and toys.

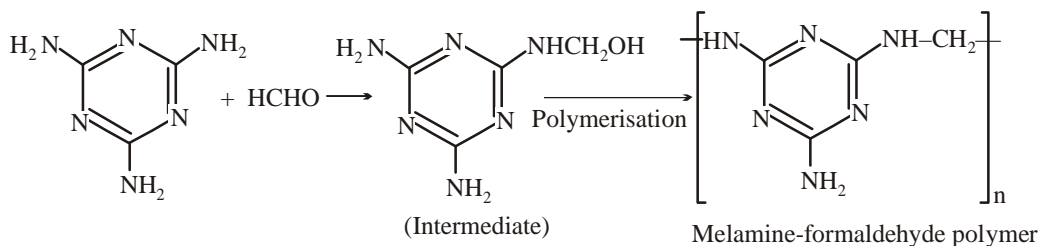
#### PLASTICISER

A plasticiser is an organic compound that dissolves in the polymer and allows the polymer chains to slide past one another. This makes polymer more flexible. Dibutylphthalate is a commonly used plasticiser.



**MELAMINE - FORMALDEHYDE RESIN**

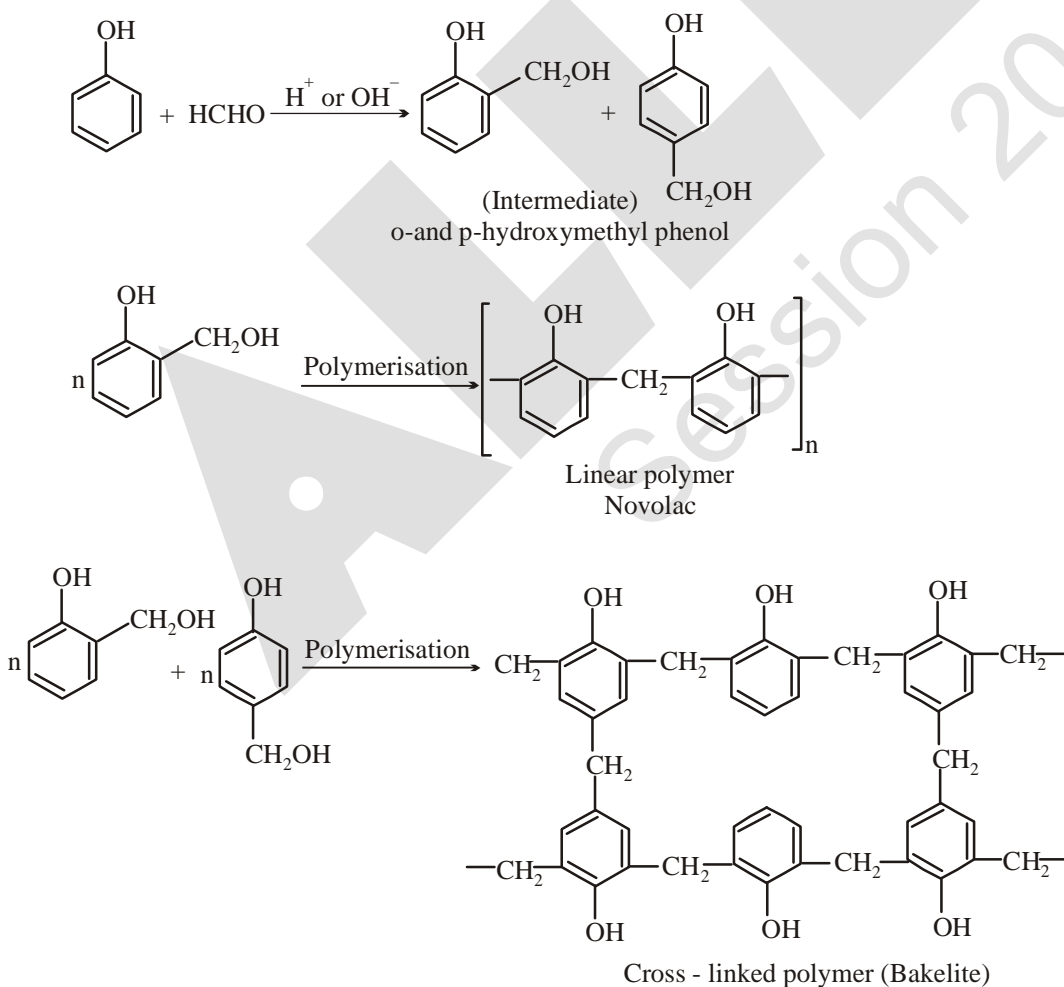
This resin is formed by condensation polymerisation of melamine and formaldehyde.



It is a quite hard polymer and is used widely for making plastic crockery under the name melamine. The articles made from this polymer do not break even when dropped from considerable height.

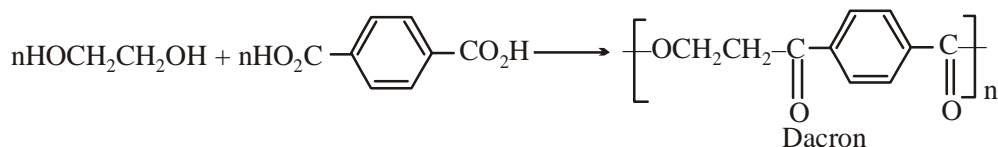
**BAKELITE**

Phenol-formaldehyde resins are obtained by the reaction of phenol and formaldehyde in the presence of either an acid or a basic catalyst. The reaction starts with the initial formation of ortho and para-hydroxymethyl phenol derivatives, which further react with phenol to form compounds where rings are joined to each other with  $-\text{CH}_2-$  groups. The reaction involves the formation of methylene bridges in ortho, para or both ortho and para positions. Linear or cross-linked materials are obtained depending on the conditions of the reaction.



## POLYESTERS

Dacron is a common polyester, prepared using ethylene glycol and terephthalic acid. The reaction is carried out at 140° to 180° C in the presence of zinc acetate and  $\text{Sb}_2\text{O}_3$  as catalyst.



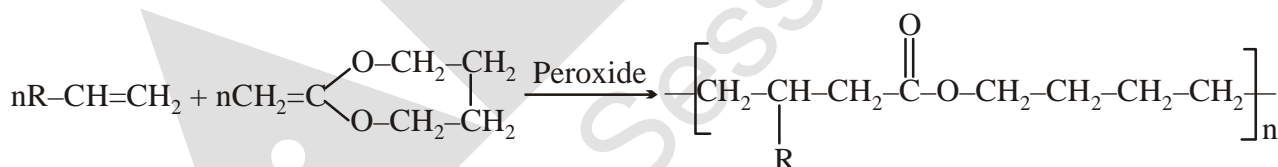
The terylene fibre (Dacron) is crease resistant and has low moisture absorption. It has high tensile strength. It is mainly used in making wash and wear garments, in blending with wood to provide better crease and wrinkle resistance.

## BIODEGRADABLE POLYMERS

By far the largest use of synthetic polymers is as plastic. A major portion of it is used as throwaway containers and packing materials. Since plastics do not disintegrate by themselves, they are not biodegradable over a period of time. Non - biodegradability is due the carbon-carbon bonds of addition polymers which are inert to enzyme catalysed reaction. These polymers create pollution problem.

Biodegradable polymers are the polymers that can be broken into small segments by enzyme catalysed reactions using enzymes produced by microorganisms. In biodegradable polymers, bonds that can be broken by the enzymes are inserted into the polymers. Therefore, when they are buried as waste, enzymes present in the ground can degrade the polymer.

One method involves inserting hydrolysable ester group into the polymer. For example, when acetal (I) is added during the polymerization of alkene, ester group is inserted into the polymeric chains.

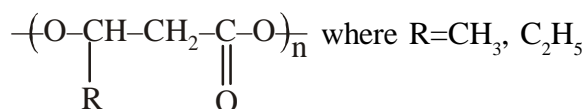
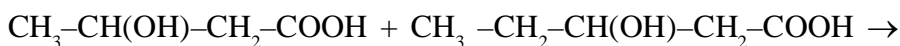


Ester linkage attacked by enzyme

Aliphatic polyesters are important class of biodegradable polymers. some examples are described below:

### (1) Poly - Hydroxybutyrate-CO-β-Hydroxyvalerate (PHBV)

It is a copolymer of 3 - hydroxybutanoic acid and 3 hydroxypentanoic acid, in which the monomer units are connected by ester linkages.





The properties of PHBV vary according to the ratio of both the acids. 3-Hydroxybutanoic acid provides stiffness and 3-hydroxypentanoic acid imparts flexibility to the co-polymer. It is used in specialty packaging, orthopaedic devices and even in controlled drug release. When a drug is put in a capsule of PHBV, It is released only after the polymer is degraded. PHBV also undergoes bacterial degradation in the environment.

## (2) POLY (GLYCOLIC ACID) AND POLY (LACTIC ACID)

They constitute commercially successful biodegradable polymers such as sutures. Dextron was the first bioadsorbable suture made for biodegradable polyesters for post - operative stitches.

## MOLECULAR MASS OF POLYMER

Normally, a polymer contains chains of varying lengths and therefore, its molecular mass is always expressed as an average. In contrast, natural polymers such as protein contains chain of identical length and hence, have definite molecular mass.

The molecular mass of a polymer is expressed as

- (a) Number average molecular mass ( $\overline{M}_n$ )

$$\overline{M}_n = \frac{\sum N_i M_i}{\sum N_i}$$

where  $N_i$  is the number of molecules of molecular mass  $M_i$

- (b) Weight average molecular mass ( $\overline{M}_w$ )

$$\overline{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

where  $N_i$  is the number of molecules of molecular mass  $M_i$ . Methods such as light scattering and ultracentrifuge depend on the mass of the individual molecules and yield weight average molecular masses.  $\overline{M}_n$  is determined by employing methods which depend upon the number of molecules present in the polymer sample viz. colligative properties like osmotic pressure.

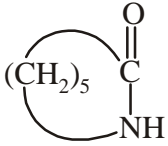
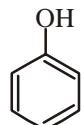
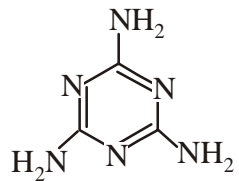
The ratio of the weight and number average molecular masses ( $\overline{M}_w / \overline{M}_n$ ) is called Poly Dispersity Index (PDI). Some natural polymers, which are generally monodispersed, the PDI is unity (i.e.  $\overline{M}_w = \overline{M}_n$ ).

In synthetic polymers, which are always polydispersed,  $PDI > 1$  because  $\overline{M}_w$  is always higher than  $\overline{M}_n$ .

## COMMON POLYMERS

| Monomer                                                                                                                                                 | Repeating unit                                                             | Polymer                                      |
|---------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------|----------------------------------------------|
| 1. $\text{CH}_2=\text{CH}_2$<br>Ethylene                                                                                                                | $-\text{CH}_2-\text{CH}_2-$                                                | Polyethylene                                 |
| 2. $\text{CH}_3-\text{CH}=\text{CH}_2$<br>Propene                                                                                                       | $-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-$                          | Polypropene                                  |
| 3. $\text{C}_6\text{H}_5-\text{CH}=\text{CH}_2$<br>Styrene                                                                                              | $-\text{CH}_2-\underset{\text{C}_6\text{H}_5}{\text{CH}}-$                 | Polystyrene                                  |
| 4. $\text{CF}_2=\text{CF}_2$<br>Tetrafluoroethylene                                                                                                     | $-\text{CF}_2-\text{CF}_2-$                                                | Polytetrafluoroethylene (PTFE), Teflon       |
| 5. $\text{CH}_2=\text{CH}-\text{Cl}$<br>Vinyl chloride                                                                                                  | $-\text{CH}_2-\underset{\text{Cl}}{\text{CH}}-$                            | Polyvinyl Chloride (PVC)                     |
| 6. $\text{CH}_2=\text{CH}-\text{CN}$<br>Vinyl cyanide or Acrylonitrile                                                                                  | $-\text{CH}_2-\underset{\text{CN}}{\text{CH}}-$                            | Polyvinyl cyanide, polyacrylonitrile, Orlon. |
| 7. $\text{CH}_2=\underset{\text{H}_3\text{C}}{\text{C}}-\overset{\text{O}}{\underset{\text{  }}{\text{C}}}-\text{O}-\text{CH}_3$<br>Methyl methacrylate | $-\text{CH}_2-\underset{\text{CH}_3}{\overset{\text{COOCH}_3}{\text{C}}}-$ | Polymethyl methacrylate, Plexiglas, Lucite   |
| 8. $\text{CH}_2=\text{CH}-\text{O}-\overset{\text{O}}{\underset{\text{  }}{\text{C}}}-\text{CH}_3$<br>Vinyl acetate                                     | $-\text{CH}_2-\underset{\text{OCOCH}_3}{\text{CH}}-$                       | Polyvinyl Acetate                            |
| 9. $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$<br>1,3-butadiene                                                                                       | $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$                            | Polybutadiene, Buna rubber                   |
| 10. $\text{CH}_2=\text{CH}-\text{Cl}$ (vinyl chloride)<br>+<br>$\text{CH}_2=\text{CCl}_2$ (Vinylidene chloride)                                         | $-\text{CH}_2-\underset{\text{Cl}}{\text{CH}}-\text{CCl}_2-\text{CH}_2-$   | Saran                                        |

|     |                                                                                                                                                                                        |                                                                                                                                                                         |                                                           |
|-----|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------|
| 11. | $\text{C}_6\text{H}_5-\text{CH}=\text{CH}_2 \text{ (Styrene)}$ $+ \text{CH}_2=\text{CH}-\text{CN} \text{ (acrylonitrile)}$                                                             | $\begin{array}{c} \text{C}_6\text{H}_5 \quad \text{CN} \\   \quad   \\ -\text{CH}_2-\text{CH}-\text{CH}-\text{CH}_2- \end{array}$                                       | SAN                                                       |
| 12. | $\text{CH}_2=\text{CH}-\text{CN} + \text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ $+ \text{C}_6\text{H}_5-\text{CH}=\text{CH}_2$                                                         | —                                                                                                                                                                       | ABS                                                       |
| 13. | $\text{CH}_2=\underset{\text{CH}_3}{\text{C}}-\text{CH}_2 + \text{CH}_2=\underset{\text{CH}_3}{\text{C}}-\text{CH}=\text{CH}_2$                                                        | —                                                                                                                                                                       | Butyl rubber                                              |
| 14. | $\text{C}_6\text{H}_5-\text{CH}=\text{CH}_2 + \text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$                                                                                             | —                                                                                                                                                                       | Buna -S, SBR                                              |
| 15. | $\text{CH}_2=\text{CH}-\text{CN} + \text{C}_6\text{H}_5-\text{CH}=\text{CH}_2$                                                                                                         | —                                                                                                                                                                       | Buna-N, NBR                                               |
| 16. | $\begin{array}{c} \text{Cl} \\   \\ \text{CH}_2=\text{C}-\text{CH}=\text{CH}_2 \\ \text{Chloroprene} \end{array}$                                                                      | $\begin{array}{c} \text{Cl} \\   \\ -\text{CH}_2-\text{C}=\text{CH}-\text{CH}_2- \end{array}$                                                                           | Neoprene                                                  |
| 17. | $\begin{array}{c} \text{COOH} \\   \\ \text{C}_6\text{H}_4 \\   \\ \text{COOH} \end{array} + \text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$                                              | $\begin{array}{c} \text{O} \quad \quad \text{O} \\    \quad \quad    \\ -\text{C}-\text{C}_6\text{H}_4-\text{C}-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}- \end{array}$ | Poly(ethylene terephthalate,<br>Terylene, Dacron or Mylar |
| 18. | $\begin{array}{c} \text{COOH} \\   \\ \text{C}_6\text{H}_4 \\   \\ \text{COOH} \end{array} + \begin{array}{c} \text{OH} \\   \\ \text{C}_6\text{H}_{10} \\   \\ \text{OH} \end{array}$ | $\begin{array}{c} \text{O} \quad \quad \text{O} \\    \quad \quad    \\ -\text{C}-\text{C}_6\text{H}_4-\text{C}-\text{O}-\text{C}_6\text{H}_{10}-\text{O}- \end{array}$ | Kodel Polyester                                           |
| 19. | $\begin{array}{c} \text{O} \\    \\ \text{C}_6\text{H}_4 \\   \\ \text{C}=\text{O} \end{array} + \text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$                                          | $\begin{array}{c} \text{O} \quad \quad \text{O} \\    \quad \quad    \\ -\text{C}-\text{C}_6\text{H}_4-\text{C}-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}- \end{array}$ | Polyethylene phthate<br>alkyd resin (Glyptal)             |

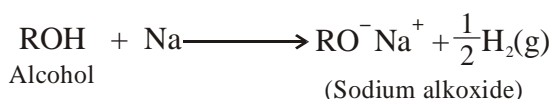
|                                                                                                                                                                                                           |                                                                                                 |                                    |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------|------------------------------------|
| <p>20. </p> <p>Caprolactam</p>                                                                                           | $-\text{NH}(\text{CH}_2)_5-\text{C}(=\text{O})-$                                                | <p>Nylon-6</p>                     |
| <p>21. <math>\text{NH}_2(\text{CH}_2)_6\text{NH}_2</math><br/>Hexamethylenediamine<br/>+<br/><math>\text{HO}-\text{C}(=\text{O})-(\text{CH}_2)_4-\text{C}(=\text{O})-\text{OH}</math><br/>Adipic Acid</p> | $-\text{NH}-(\text{CH}_2)_6-\text{NH}-\text{C}(=\text{O})-(\text{CH}_2)_4-\text{C}(=\text{O})-$ | <p>Nylon - 66</p>                  |
| <p>22.  + HCHO</p>                                                                                                       | <p>—</p>                                                                                        | <p>Bakelite or resol</p>           |
| <p>23. <math>\text{NH}_2-\text{C}(=\text{O})-\text{NH}_2</math> + HCHO</p>                                                                                                                                | <p>—</p>                                                                                        | <p>Urea- formaldehyde resin</p>    |
| <p>24.  + HCHO</p> <p>Melamine</p>                                                                                     | <p>—</p>                                                                                        | <p>Malamine formaldehyde resin</p> |

## CHEMICAL TESTS FOR FUNCTIONAL GROUPS

- Elemental analysis, physical, spectral and solubility test give a reasonable idea regarding the identity of unknown compound.
- Despite the tremendous importance and ease of spectral analysis, chemical tests are indispensable to complete characterization.

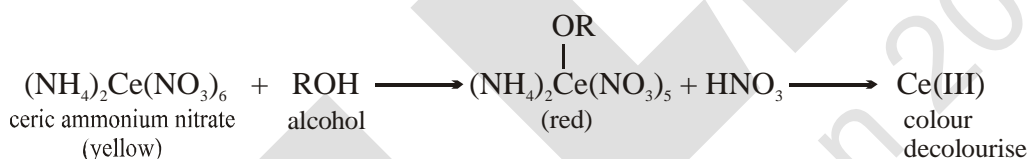
## 1. Test For Alcohols :

## (i) Sodium Metal



- When Na-metal reacted with alcohol  $\text{H}_2(\text{g})$  evolve
- It occurs in  $1^\circ$ ,  $2^\circ$  &  $3^\circ$
- The rate is highly variable and depends upon the alcohol structure.
- Other Functional groups that evolve  $\text{H}_2(\uparrow)$   
 $\text{R}_2\text{NH}$ ,  $\text{RSH}$ ,  $\text{RC}\equiv\text{C-H}$ ,  $\text{RCO}_2\text{H}$  etc.

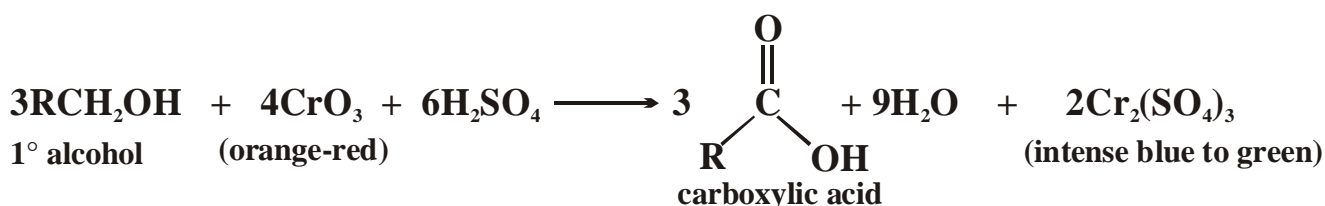
## (ii) Ceric Ammonium Nitrate Oxidation (CAN Test)

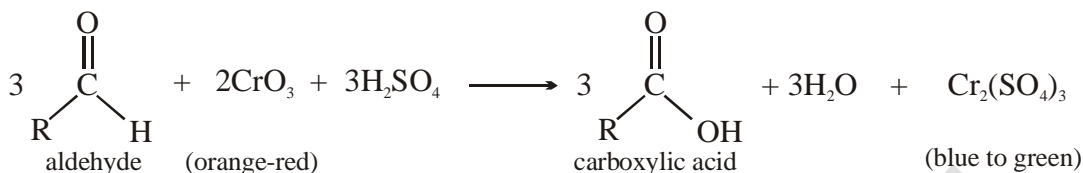
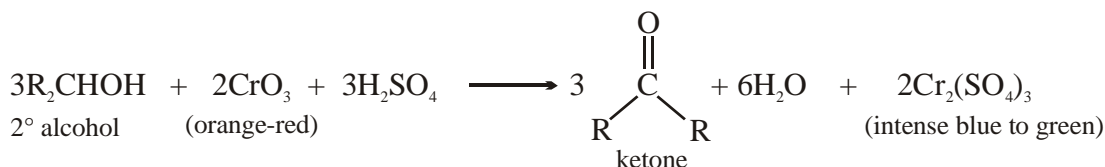


- Positive Test:** Color changes from yellow to red first then to colorless solution. (1 min. to 12 hrs)
- A positive test includes successively the formation, and then the disappearance of the red color.
- Very good test for  $1^\circ$ ,  $2^\circ$  alcohol, but slow for  $3^\circ$  alcohol
- Note:** Phenols gives brown or black colour.

(iii) Jones Oxidation: Chromic anhydride or Chromium Trioxide ( $\text{CrO}_3$ )

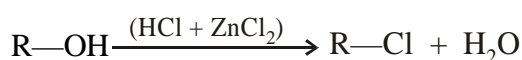
- A positive test for  $1^\circ$ , and  $2^\circ$  alcohols consists in the changes from an orange-red color ( $\text{Cr}^{6+}$ ) to opaque suspension with green to blue color ( $\text{Cr}^{3+}$ ) in 2 sec.
- $3^\circ$  alcohols give no visible reaction within 2 sec. remaining orange
- Note:** Aldehydes give positive result.





**(iv) Lucas Test**

- This test distinguishes 1°, 2° & 3° alcohol from each other
- It uses, anhydrous  $\text{ZnCl}_2$  in conc.  $\text{HCl}$  (lucas reagent)



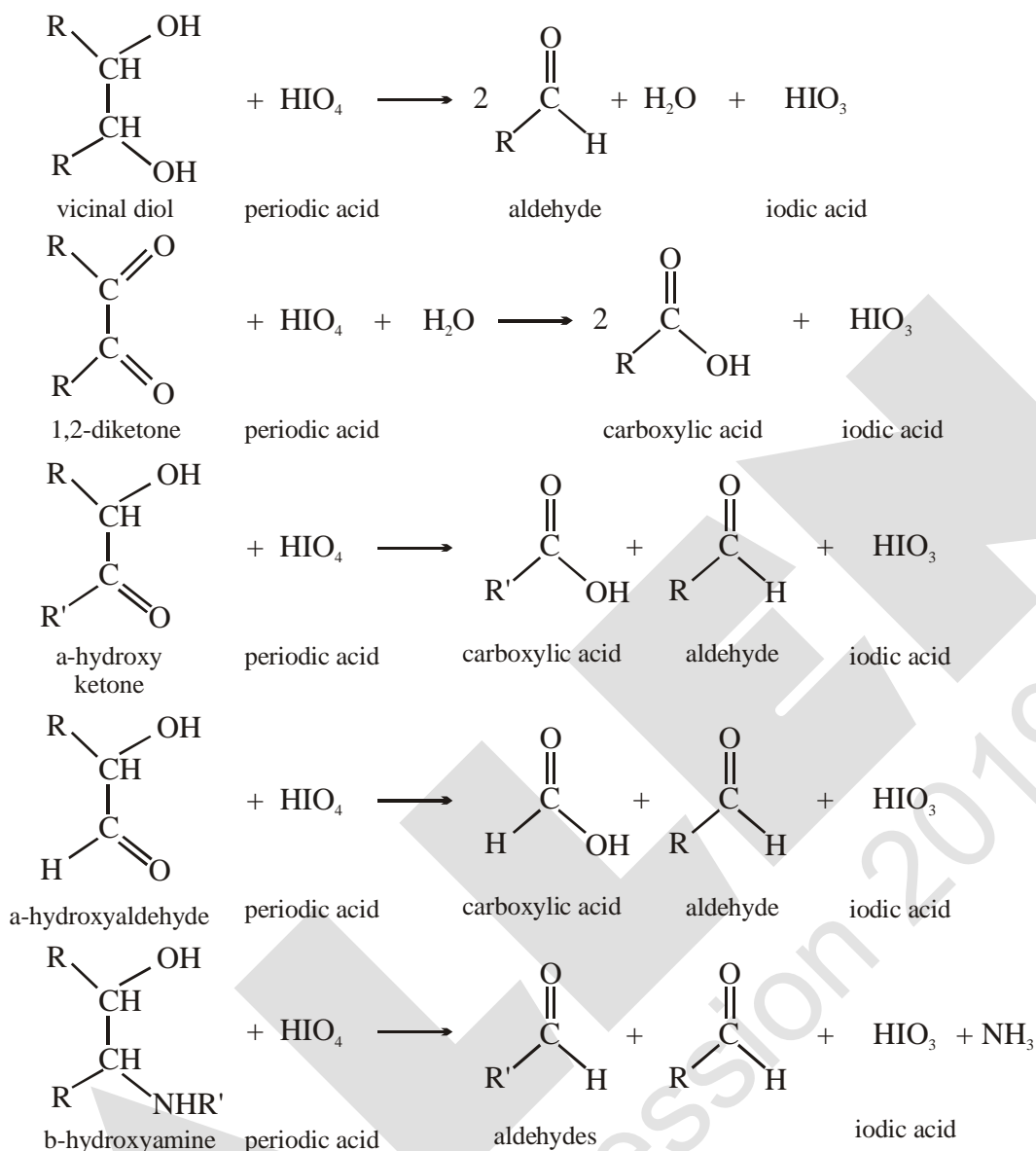
- 3° alcohols give white turbidity solution immediately
- 2° alcohols give white turbidity solution within 5 to 10 minutes
- 1° alcohols does not give white turbidity at room temperature

**Note :** Benzyl alcohol also react immediately

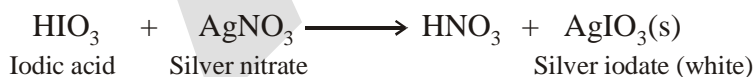
**(v) Victor-Mayer Test**

- This test also distinguishes 1°, 2° & 3° alcohol

| 1° - Alcohol                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | 2° - Alcohol                                                                                                                                                                                                                                                                                                                                                                                                      | 3° - Alcohol                                                                                                                                                                                                                                     |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| $\begin{array}{c} \text{R-CH}_2\text{-OH} \\ \downarrow \text{Red P + I}_2 \\ \text{R-CH}_2\text{-I} \\ \downarrow \text{NaNO}_2 \\ \text{R-CH}_2\text{-N} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{O} \end{array} \\ \downarrow \text{HNO}_2 \\ \text{R-C} \begin{array}{l} \nearrow \text{O} \\ \parallel \\ \text{N-OH} \end{array} \\ \text{(Nitrolic Acid)} \\ \downarrow \text{NaOH} \\ \text{R-C} \begin{array}{l} \parallel \\ \text{N-O}^\ominus \text{Na}^\oplus \end{array} \\ \text{(Red colour)} \end{array}$ | $\begin{array}{c} \text{R} \\   \\ \text{R-CH-OH} \\ \downarrow \text{Red P + I}_2 \\ \text{R} \\   \\ \text{R-CH-I} \\ \downarrow \text{NaNO}_2 \\ \text{R} \\   \\ \text{R-CH-NO}_2 \\ \downarrow \text{HNO}_2 \\ \text{R} \\   \\ \text{R-C} \begin{array}{l} \nearrow \text{O} \\ \parallel \\ \text{N=O} \end{array} \\ \text{(Pseudo nitro)} \\ \downarrow \text{NaOH} \\ \text{(Blue colour)} \end{array}$ | $\begin{array}{c} \text{R} \\   \\ \text{R-C-OH} \\ \downarrow \text{Red P + I}_2 \\ \text{R} \\   \\ \text{R-C-I} \\ \downarrow \text{NaNO}_2 \\ \text{R} \\   \\ \text{R-C-NO}_2 \\ \downarrow \text{HNO}_2 \\ \text{No Reaction} \end{array}$ |

(vi) Periodic Acid ( $\text{HIO}_4$ ) Test for detection of Vicinal Diols and Related Compounds

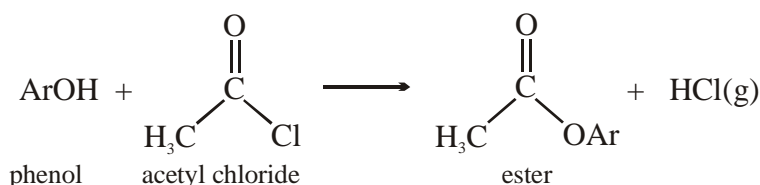
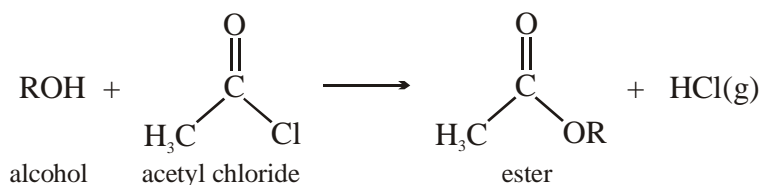
- The iodic acid is detected with 5%  $\text{AgNO}_3$  solution -an immediate precipitation of silver iodate occurs.



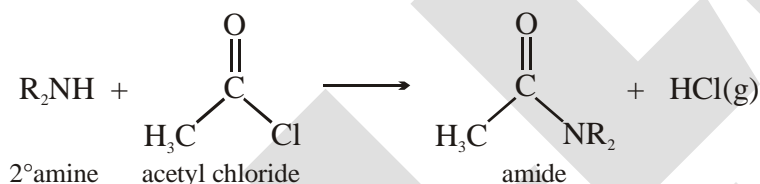
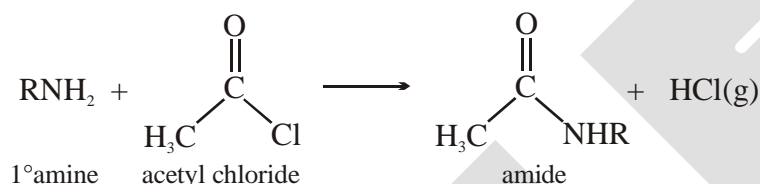
- Olefins,  $2^\circ$  alcohols, 1,3-glycols, ketones and aldehydes are not affected by  $\text{HIO}_4$  under the test condition.

(vii) Acetyl Chloride

- Positive Test: Evolution of HCl gas and formation of ester as a top layer

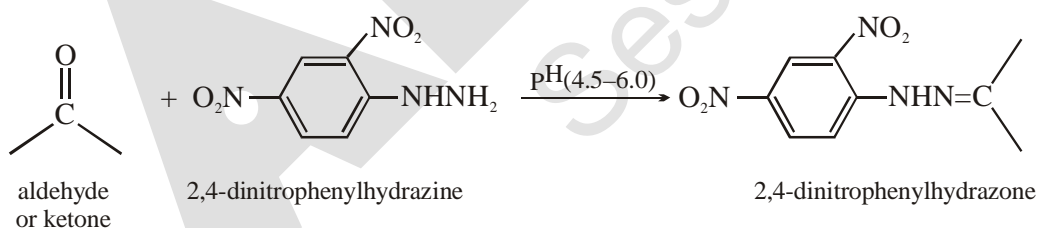


- 3° alcohols form primarily alkyl chloride due to the reaction of the liberated HCl on another molecule of the alcohol.
- Other functional groups that give positive test: 1° and 2° amines



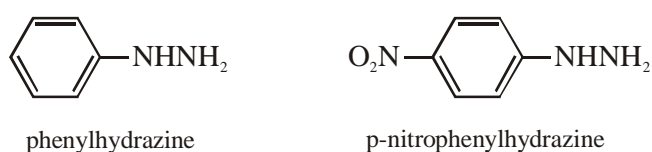
## 2. Classification Tests For Aldehydes and Ketone

### (i) 2,4-Dinitrophenyl Hydrazine



- Positive Test:** formation of yellow, orange or red ppt.
- The precipitate may be oily at first and become crystalline on standing.

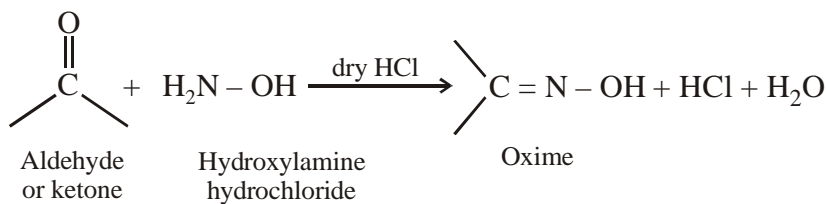
### (ii) Phenyl hydrazine and p-Nitrophenyl hydrazine.





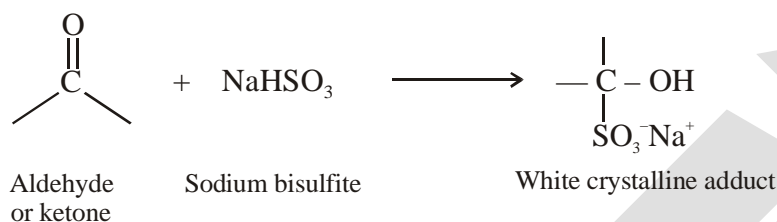
**Positive Test: formation of yellow ppt.**

**(iii) Hydroxylamine Hydrochloride**



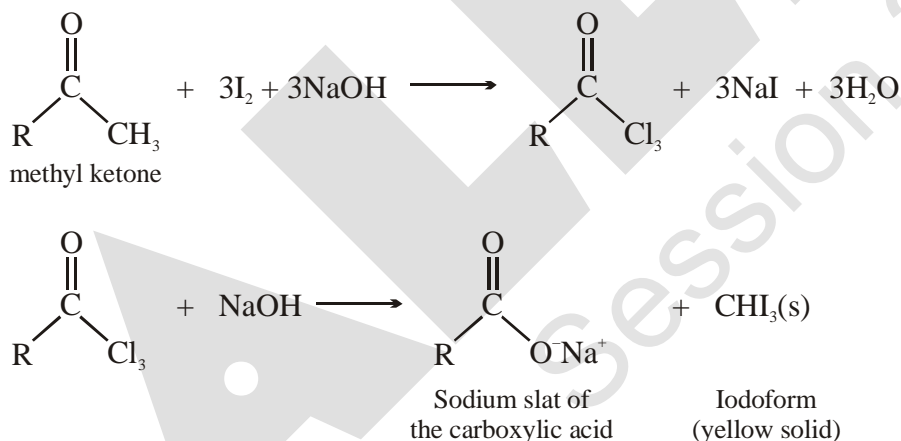
The liberation of hydrogen chloride can be detected by the change in colour from orange to red of a pH indicator.

**(iv) Sodium Bisulfite (NaHSO<sub>3</sub>)**

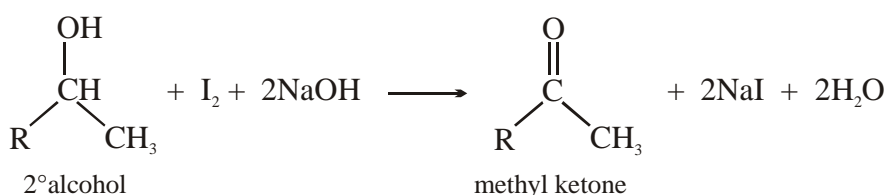


- **Positive Test:** By aldehydes and methyl ketone
- Only some cyclic ketones give positive results (ppt)
- This reaction is greatly inhibited by the steric constraints about the carbonyl group.

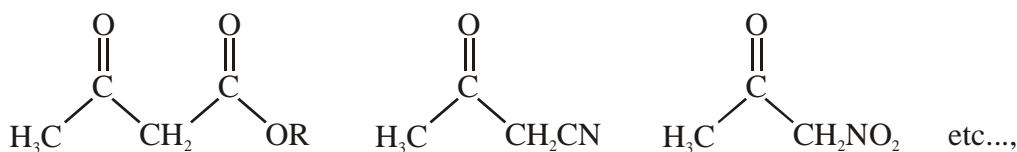
**(v) Iodoform Test (For Methyl Ketones)**



- **Positive Test:** Yellow ppt for methyl ketones
- **Disadvantages:** Some compounds that can be easily oxidized to methyl ketones give also positive results
- The principal types of compounds that give a positive test:

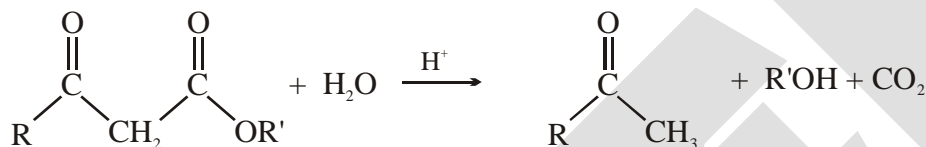
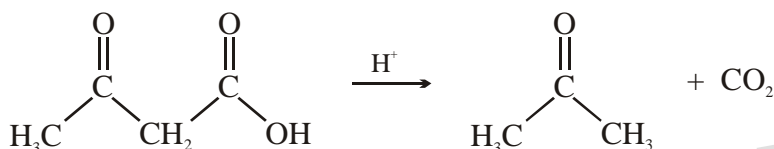


- The test is negative for the following type:



In such compounds the reagent removes the acetyl group and converts it to acetic acid, which resists iodination.

Acetoacetic acid is unstable, acidic aqueous solutions decompose to give  $\text{CO}_2$  and acetone.



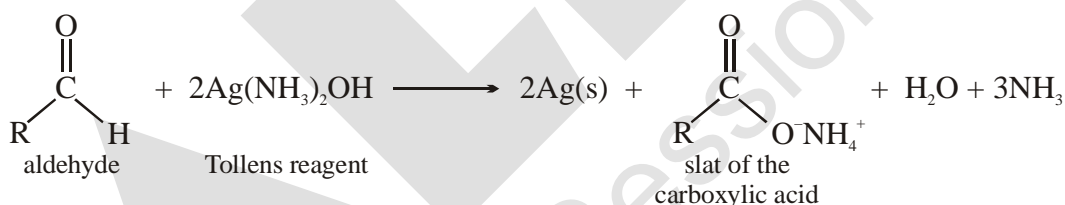
give positive iodoform test

### 3. Tests that give positive results with aldehydes and negative results with Ketones

- (i) **Jones Oxidation: Chromic anhydride or Chromium Trioxide ( $\text{CrO}_3$ )**

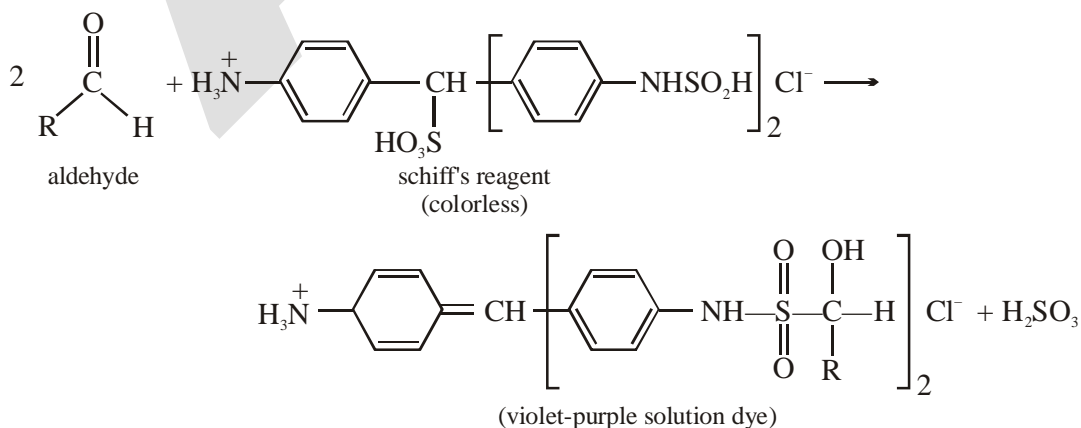
(Refer Jones Oxidation for alcohols at Page No. 22)

- (ii) **Tollens Reagents  $\text{Ag}(\text{NH}_3)_2\text{OH}$**



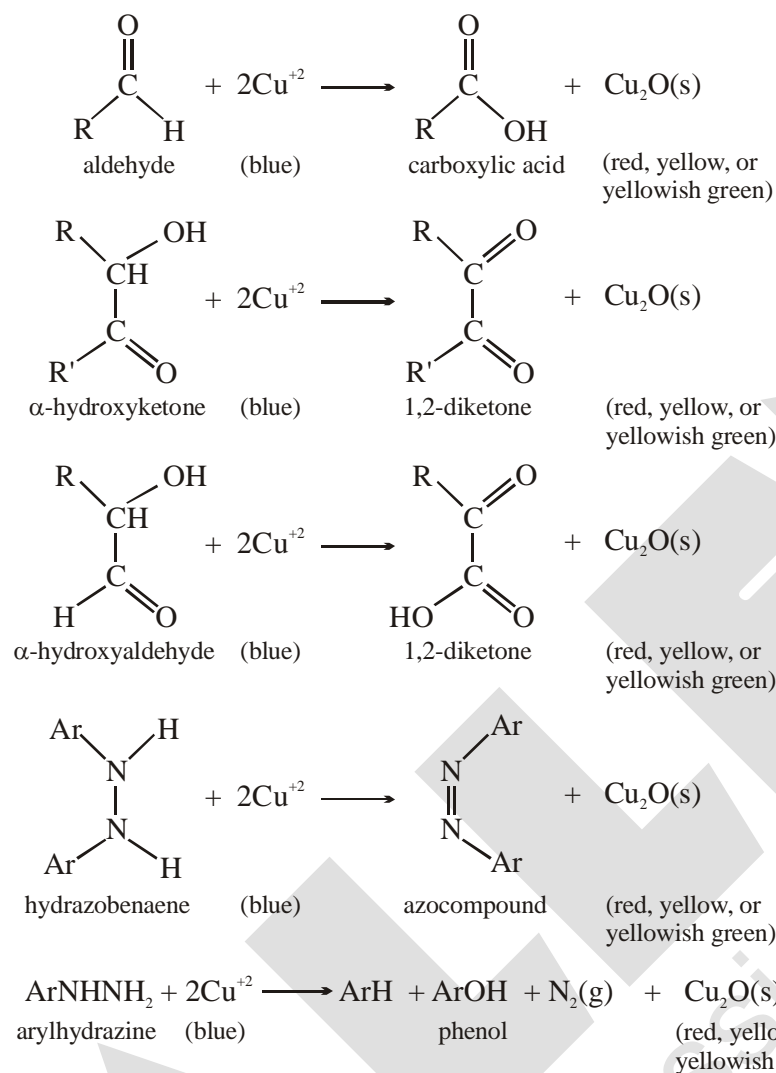
- Positive Test:** Formation of silver mirror (Ag) or colloidal (granular) gray or black Ag precipitate.

- (iii) **Schiff's Reagent**

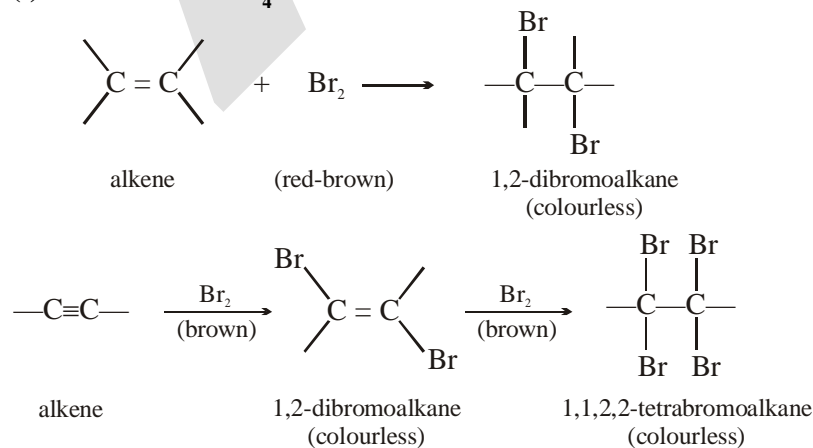


(iv) **Bendicts solution and Fehling's Solution**

- **Positive Test:** yellow or yellowish green ppt.
- All aldehydes give positive result except aromatic aldehydes (negative)

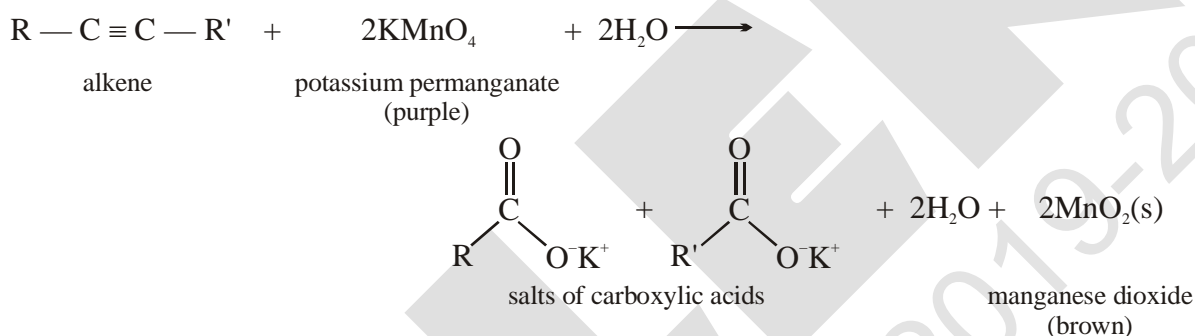
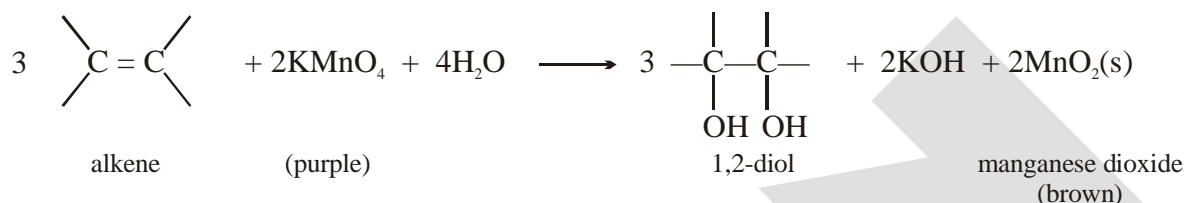
**4. Classification Tests for Unsaturation "alkenes & alkynes"**

- Alkanes are not usually characterized chemically because they are quite inert to most classification reactions

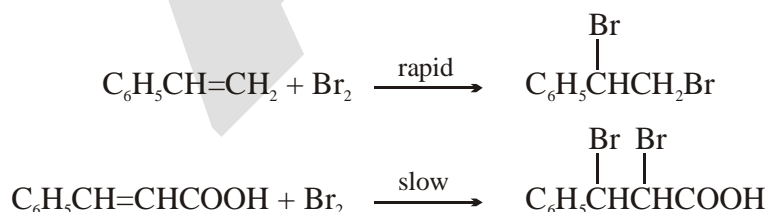
**(i) Bromine in CCl<sub>4</sub>**

- **Positive Test:** Bromine color discharged without evolution of gas (HBr)
- Alkenes & alkynes give positive results
- If HBr is evolved, it indicates phenols, enols & enolizable compounds, -,
- Bromine color is discharged by amines to produce a salt, which could be mistaken for addition.

(ii) **Baeyer Test (KMnO<sub>4</sub> aqueous)**



- **Positive Test:** Purple color discharges, and brown color ppt (MnO<sub>2</sub>) appears
- **Note :** Aldehydes and alcohols also give positive result
- Since the ionic characters of the Br<sub>2</sub> and KMnO<sub>4</sub> reactions are very different, there is some complementary character between the two tests.
- For example, some alkenes bearing electron-withdrawing groups undergo rapid reaction with KMnO<sub>4</sub> but often slow or negligible reaction with Br<sub>2</sub>.



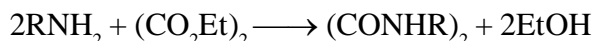
- A few tetrasubstituted olefins such as C<sub>6</sub>H<sub>5</sub>CBr=CBrc<sub>6</sub>H<sub>5</sub> and (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>C=C(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> fail to give positive tests with Br<sub>2</sub> in CCl<sub>4</sub> or KMnO<sub>4</sub> solution.



## 6. Tests for Amines and Amine Salts

### (i) Diethyl oxalate test :

- This method helps in the separation of primary, secondary and tertiary amines.
- Primary amines on reaction with diethyl oxalate gives solid oxamide, secondary amine gives liquid oxamic ester and tertiary amine remains unreacted in gaseous form.

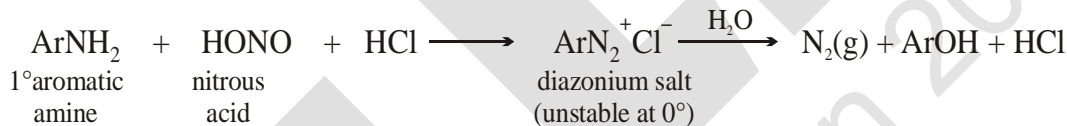
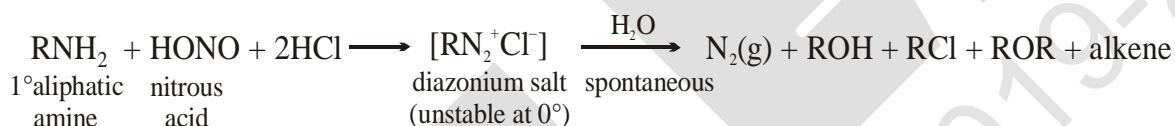


- The gaseous tertiary amine is separated out.
- The solid oxamide is filtered out of the liquid oxamic ester.
- These products are added to the alkaline solution of NaOH.

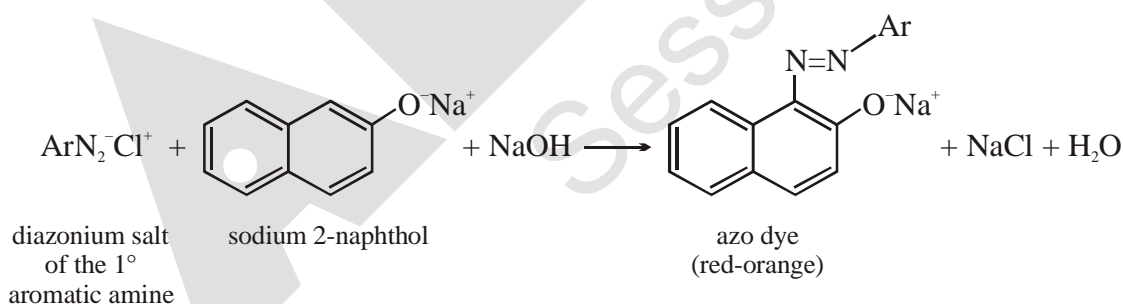
In this way, Primary, secondary and tertiary amines are separated by Hoffmann's Method

### (ii) Nitrous Acid

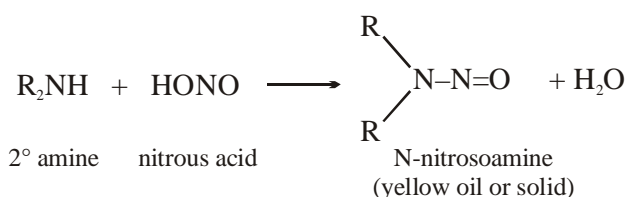
- Reaction of amines with nitrous acid (HONO) classifies the amine not only as 1°, 2°, or 3°, but also as aliphatic or aromatic.



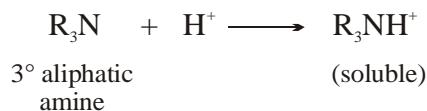
- The diazonium salt of the primary aromatic amine reacts with sodium 2-naphthol to produce a red-orange azo dye.



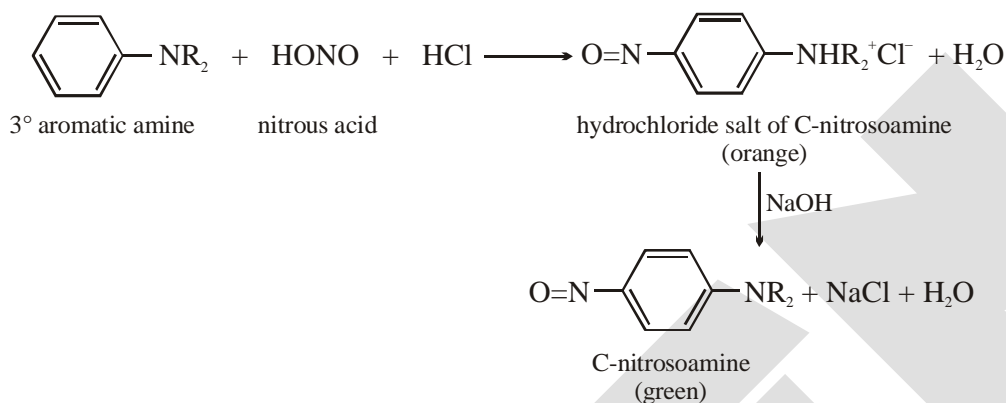
- 2° amines undergo a reaction with nitrous acid to form N-nitrosoamine, which are usually yellow solids.



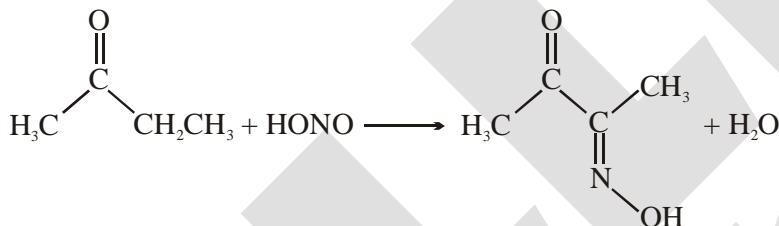
- 3° aliphatic amines do not react with nitrous acid, but they form a soluble salt. The reaction mixture gives an immediate positive test on the starch-iodide paper for nitrous acid.



- 3° aromatic amines react with nitrous acid to form the orange-colored hydrochloride salt of the C-nitrosoamine. Treating the solution with base liberates the blue or green C-nitrosoamine.

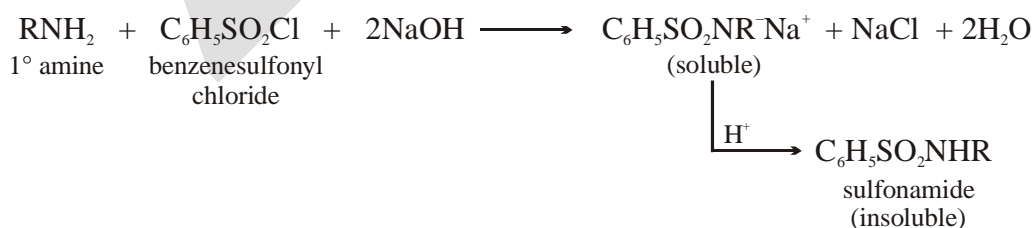


- Although nitrous acid is useful for characterizing amines, other functional groups also react.
- A methylene group adjacent to a keto group is converted to an oximino group and alkyl mercaptans yield red S-alkyl thionitrites.

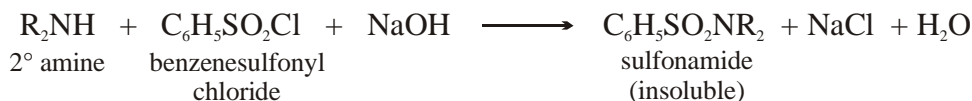


### (iii) Hinsberg Test

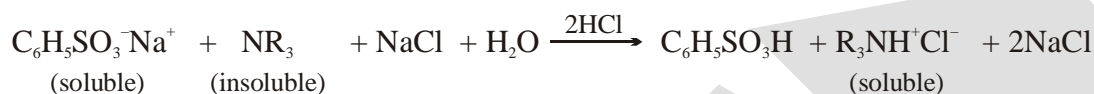
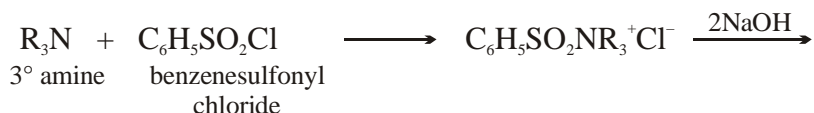
- Based on the reaction of the amine with benzenesulfonyl chloride (Hinsberg reagent), it can be used to separate 1°, 2°, and 3° amines.
- 1° amines: give solution that produce ppt after addition of HCl



2° amines: give ppt - acidification of the solution does not dissolve the sulfonamide (i.e., the PPT is not soluble in NaOH or HCl)



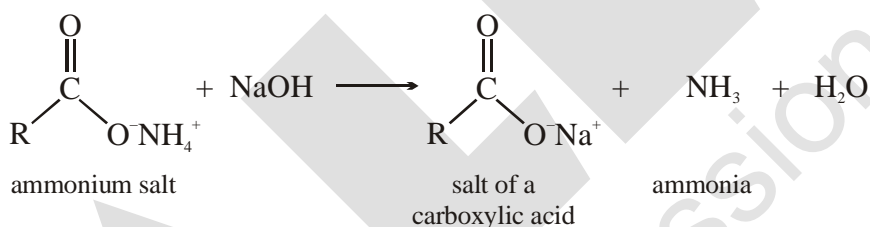
- 3° amines: undergo reaction with benzenesulfonyl chloride to produce quaternary ammonium sulfonate salts, which yield sodium sulfonate and insoluble 3° amines in basic solution.
- Acidification of the reaction mixture results in the formation of sulfonic acids and soluble amine salts



- The results of the Hinsberg test must not be used alone in classifying amines. The solubility of the original compounds must also be considered.
- If the original compound is amphoteric, which means that it is soluble in both acids and alkalies, the Hinsberg method fails to distinguish among the types of amines.

#### (iv) Sodium Hydroxide Treatment of Ammonium Salt and Amine Salts

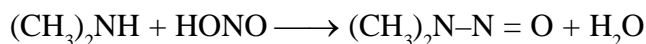
- Amine salts can be detected by treating the salt with NaOH to liberate ammonia or amine.



- Moistened pink litmus paper placed in the vapor above the solution will turn blue if ammonia or a volatile amine is present.

#### (v) Libermann's nitroso test :

It is used as a test for secondary amines. Secondary amines (aliphatic as well as aromatic) reacts with nitrous acid to form N-nitrosoamines.

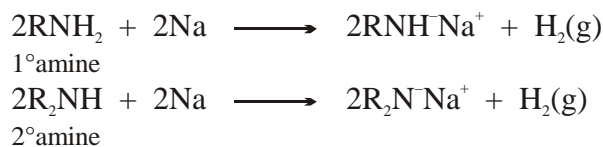


- Nitrosoamines are water soluble yellow oils and when warmed with phenol and few drops of conc.  $\text{H}_2\text{SO}_4$  produce a green colour solution which turns blue on adding alkali. This reaction is called Libermann's nitroso reaction.
- Tertiary amine do not react with nitrous acid.

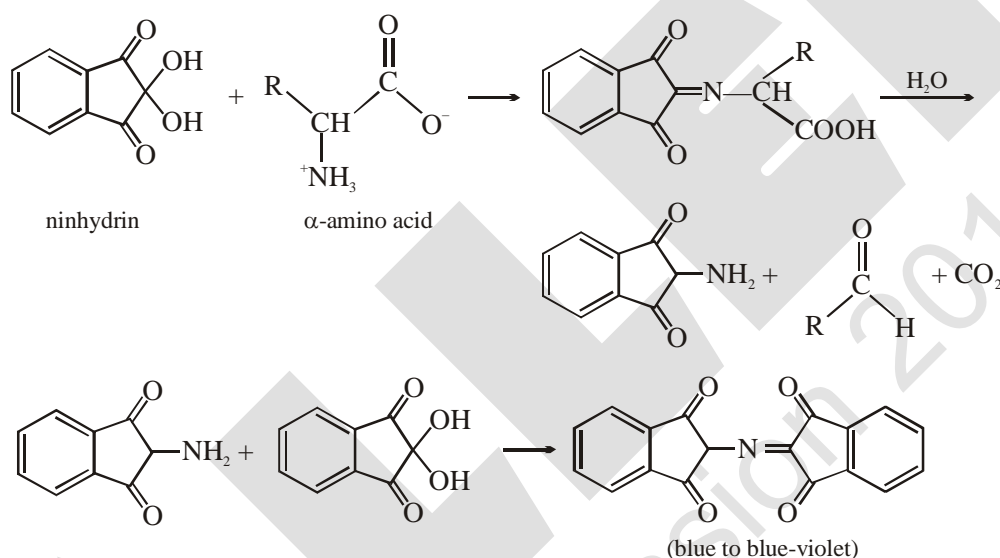


**Sodium Metal :**

- The active hydrogen on 1° and 2° amines undergo reaction with sodium to form salt and liberate hydrogen gas

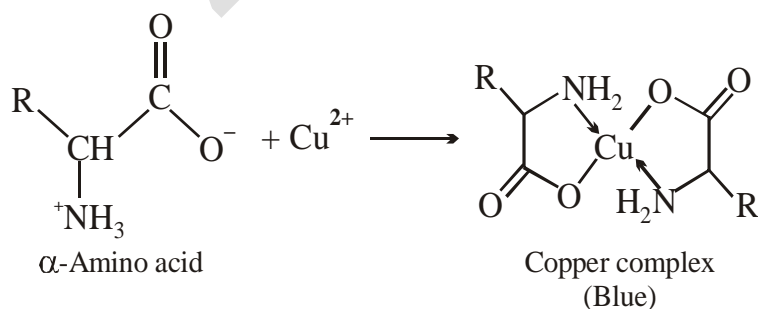
**7. Tests for Amino Acids****(i) Ninhydrin Test :**

- Amino acids and  $\alpha$ -amino acids react with ninhydrin to give a positive test which is blue or blue-violet color.



- Ammonium salts ( $\text{NH}_4^+ \text{Cl}^-$ ) give a positive test.
- Some amines, such as aniline, yield orange to red colors, which is considered a negative test.
- Proline, hydroxyproline, and 2-, 3-, and 4-aminobenzoic acids fail to give

**Blue colour but produce a yellow color instead.**

**(ii) Copper Complex Formation**

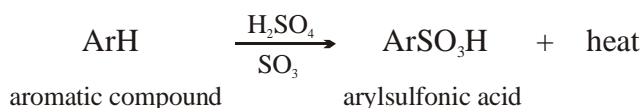
- Reaction with copper(II) sulfate solution yields a moderate-to deep-blue liquid or a dark-blue solid.

## 8. Tests for Aromatics

- If the molecule already contains reactive chemical substituents (acids, amines, ethers, carbonyl compounds, etc.,) use the corresponding classification test for that particular group.
- New substituents can be added onto the aromatic ring or existing substituents can be modified, such that the new

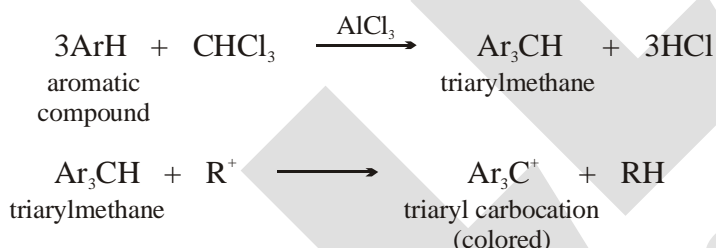
### Compound May be More Readily Characterized.

#### (i) Fuming Sulfuric Acid



- This test is good for aromatics with no other functional groups.
- Positive Test: the aromatic compound dissolves completely in  $\text{H}_2\text{SO}_4$  with the evolution of heat (Fuming)

#### (ii) Chloroform and Aluminum Chloride



- Aromatics give colored solution or powder.
- Positive Test: (Orange, red, blue, purple, green)
- Non aromatics give yellow color (Negative result)

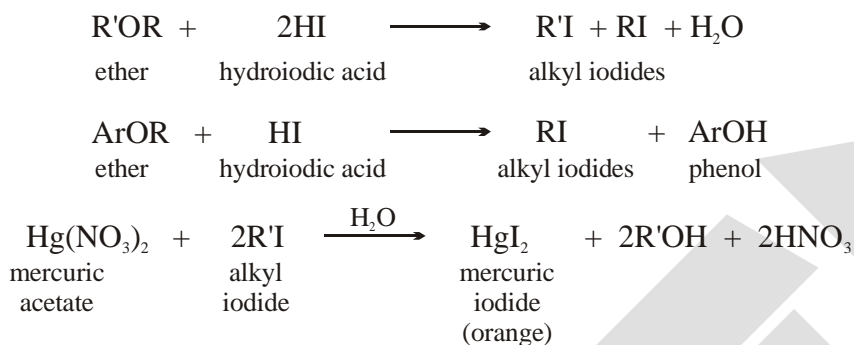
#### (iii) Azoxybenzene and Aluminum Chloride

- The color of the solution or precipitate is dependent on the functional groups present on the aryl group.
- Aromatic hydrocarbons and their halogen derivatives produce a deep-orange to dark-red color in solution or give a precipitate.
- Fused aromatic ring (such as naphthalene, anthracene, and phenanthrene) produce brown color.
- Aliphatic hydrocarbons give no color or, at most, a pale yellow.

## 9. Tests for Ethers

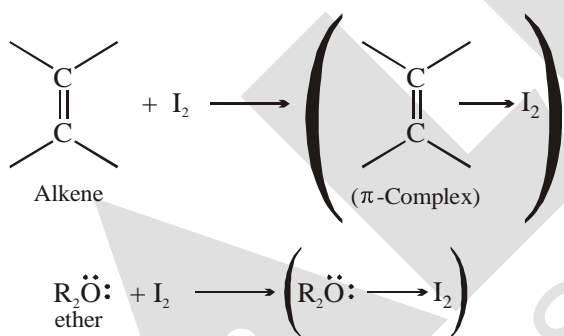
- Ethers are only a little more polar and slightly more reactive than either saturated hydrocarbons or alkyl halides
- Ethers form extremely explosive peroxides upon standing, specially when exposed to air and/or light. Liquid ethers that shows solid precipitates should not be handled.

### (i) Hydroiodic Acid (Zeisel's, Alkoxy method)



- Positive Test: Orange or Orange-red color indicating.
- Note: Ethyl and methyl esters give also positive result.

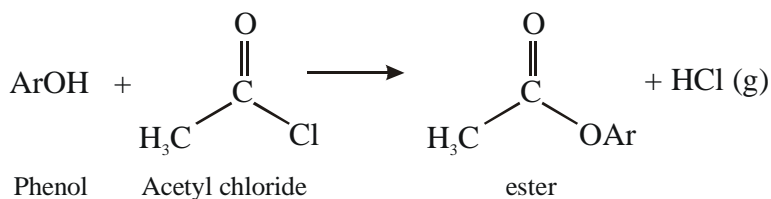
### (ii) Iodine Test for Ethers and Unsaturated Hydrocarbons



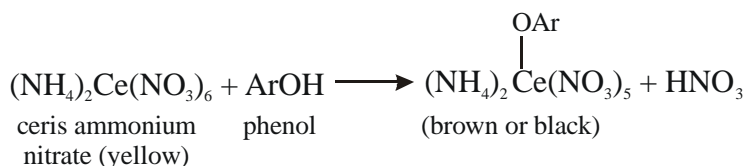
- Positive test: the color of the solution changes from purple to tan.
- Aromatic hydrocarbons, saturated hydrocarbons, fluorinated hydrocarbons and chlorinated hydrocarbons do not react.
- Unsaturated hydrocarbons produce a light-tan solid, while retaining the purple color of the iodine solution.

## 10. Tests for Phenols

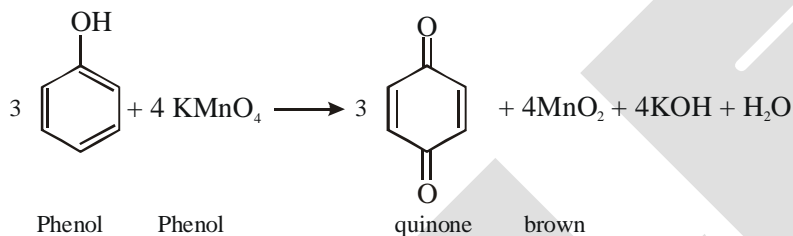
- As with alcohols, the acidic hydrogen in phenol can be detected with sodium (hydrogen gas is evolved) or with acetyl chloride (an ester layer is formed).



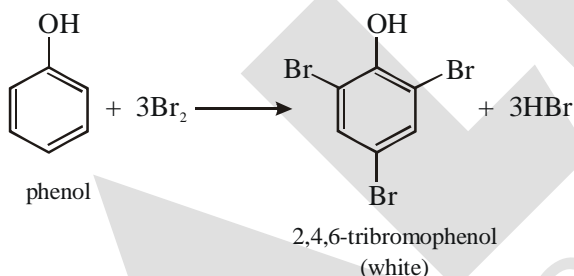
- Phenols undergo reaction with yellow ceric ammonium nitrate to produce brown or black products.



- Phenols reduce potassium permanganate solution and undergo oxidation to quinones.
- The manganese is reduced from +7 which gives a purple solution to +4 which is brown.

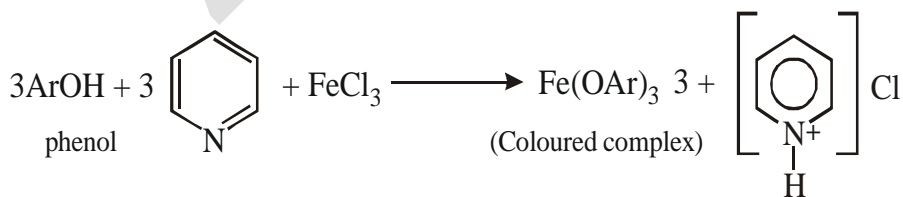


(i) **Bromine water**



- Positive Test: decolorization of bromine.
- This is good for water soluble phenols

(ii) **Ferric Chloride - Pyridene Reagent**

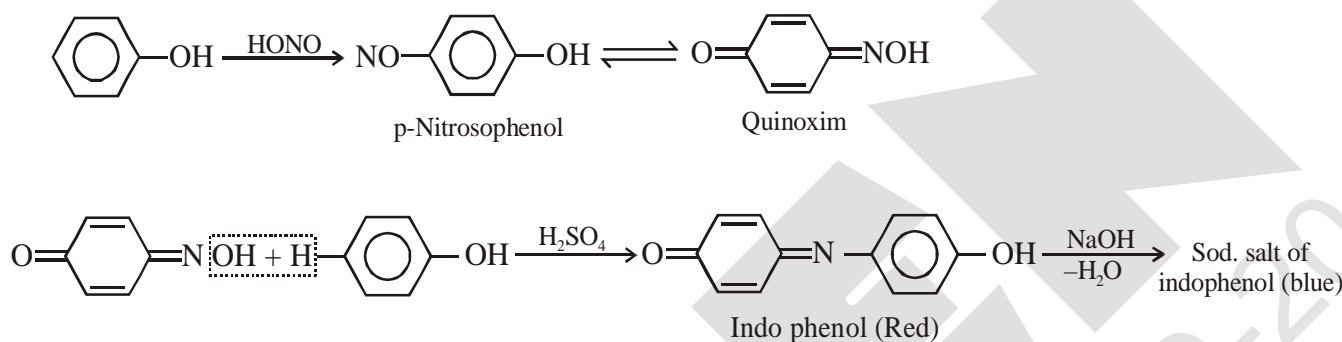


- Positive Test: Production of blue, violet, purple, green, or red-brown colors

- Good for all types of Ar-OH.
- Positive test for enols.  $\left( \begin{array}{c} \text{OH} \\ | \\ \text{C}=\text{C}-\text{C}(=\text{O})\text{R} \end{array} \right)$
- Carboxylic acid with  $\text{FeCl}_3$  gives red colour only when saturating with  $\text{NH}_3$ .

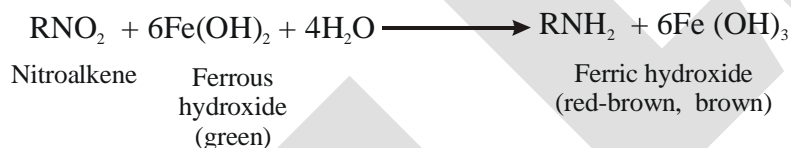
(iii) **Libermann's nitroso test :**

While phenol is reacted with  $\text{NaNO}_2$  and concentrated  $\text{H}_2\text{SO}_4$ , it provides a deep green colour which changes to red on dilution with water. while generated alkaline along with  $\text{NaOH}$ , blue colour is restored. This reaction is termed as Liebermann's nitroso reaction and is employed as a test of phenol.



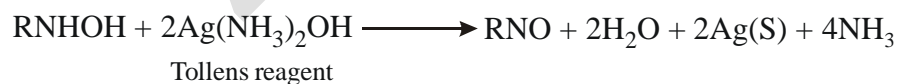
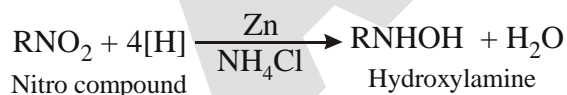
## 11. Test For Nitro Compounds

### (i) Ferrous Hydroxide Reduction



- Positive Test: indicated by the change in color from green to red-brown or brown due to the oxidation of iron from +2 to +3.
- A negative test is indicated by a greenish precipitate.
- Note: Nitroso compounds, quinones, hydroxylamines alkyl nitrates give also positive results

### (ii) Zinc and Ammonium Chloride Reduction

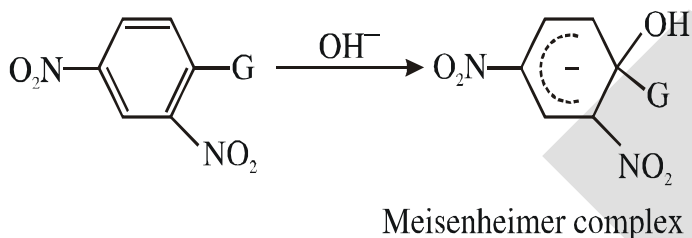


- Test the solution with Tollens Reagent
- **Positive Test:** formation of metallic silver
- Only 3° aliphatic nitro compounds and aromatic nitro compounds are reduced by  $\text{Zn}/\text{NH}_4\text{Cl}$  to the hydroxylamine.

- The hydroxylamine is then detected by the formation of metallic silver in the Tollens test (or formation of a black or grey precipitate). This is known as Mulliken–baker test:.

**(iii) Treatment of Aromatic Compounds with Sodium Hydroxide**

- The number of nitro groups on an aromatic ring can be determined by the reaction with NaOH
- In the reaction with NaOH:
- Mononitro aromatic compounds yield no color change or a very light yellow
- Dinitro aromatic compounds produce a bluish-purple color
- Trinitro aromatic compounds give a red color
- The color of the solution is due to a Meisenheimer complex



## (A) ELEMENTAL ANALYSIS

### *Lassaigne method (Detection of elements)*

| Element                       | Sodium Extract (S.E.)                                                                 | Confirmed Test                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | Reactions                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |
|-------------------------------|---------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Nitrogen                      | $\text{Na} + \text{C} + \text{N} \xrightarrow{\Delta} \text{NaCN}$ (S.E.)             | S.E. + $\text{FeSO}_4 + \text{NaOH}$ ,<br>boil and cool,<br>+ $\text{FeCl}_3$ + conc. $\text{HCl}$<br>Blue or green colour<br>(i) S.E. + sodium nitro<br>prusside (A)<br>A deep violet colour.<br>(ii) S.E. + $\text{CH}_3\text{COOH}$<br>+ $(\text{CH}_3\text{COO})_2\text{Pb}$<br>A black ppt.<br>S.E. + $\text{HNO}_3 + \text{AgNO}_3$<br>(i) White ppt. soluble<br>in aq $\text{NH}_3$ confirms Cl<br>(ii) Yellow ppt<br>partially soluble in<br>aq. $\text{NH}_3$ confirm Br<br>(iii) Yellow ppt<br>insoluble in aq $\text{NH}_3$<br>confirms I<br>As in test for nitrogen;<br>instead of green or blue<br>colour, blood red<br>coloration confirms<br>presence of N and S<br>both | $\text{FeSO}_4 + 2\text{NaOH} \longrightarrow \text{Fe}(\text{OH})_2 + \text{Na}_2\text{SO}_4$<br>$\text{Fe}(\text{OH})_2 + 6\text{NaCN} \longrightarrow \text{Na}_4[\text{Fe}(\text{CN})_6] + 2\text{NaOH}$<br>$3\text{Na}_4[\text{Fe}(\text{CN})_6] + 4\text{FeCl}_3 \xrightarrow{\text{HCl}} \text{Fe}_4[\text{Fe}(\text{CN})_6]_3 + 12\text{NaCl}$<br>Prussian blue<br>(i) $\text{Na}_2\text{S} + \text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \longrightarrow \text{Na}_4[\text{Fe}(\text{CN})_5\text{NOS}]$<br>(A) deep violet<br>(ii) $\text{Na}_2\text{S} + (\text{CH}_3\text{COO})_2\text{Pb} \xrightarrow{\text{CH}_3\text{COOH}} \text{PbS} \downarrow + 2\text{CH}_3\text{COONa}$<br>black ppt. |
| Sulphur                       | $2\text{Na} + \text{S} \xrightarrow{\Delta} \text{Na}_2\text{S}$ (S.E.)               |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |
| Halogen                       | $\text{Na} + \text{Cl} \xrightarrow{\Delta} \text{NaCl}$ (S.E.)                       |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | $\text{NaX} + \text{AgNO}_3 \xrightarrow{\text{HNO}_3} \text{AgX} \downarrow$<br>ppt<br>$\text{AgCl} + 2\text{NH}_3(\text{aq}) \longrightarrow [\text{Ag}(\text{NH}_3)_2]\text{Cl}$<br>white ppt soluble                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |
| Nitrogen and Sulphur together | $\text{Na} + \text{C} + \text{N} + \text{S} \xrightarrow{\Delta} \text{NaCNS}$ (S.E.) |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | $\text{NaCNS} + \text{FeCl}_3 \longrightarrow [\text{Fe}(\text{CNS})]\text{Cl}_2 + \text{NaCl}$<br>blood red colour                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |

**CARBONYL COMPOUND,  
ALDOL & SIMILAR NAME REACTIONS**



**ALLEN**  
Session 2019-20

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## CARBONYL COMPOUND

## EXERCISE # I

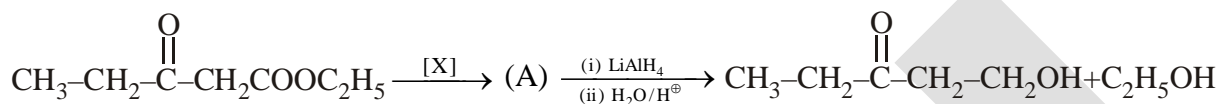
Q.1 Arrange these compounds in decreasing order of reactivity for the nucleophilic attack :

- (I) Acid chloride                  (II) Aldehyde                  (III) Ketone                  (IV) Ester

Select the correct answer from the codes given below :

- (A)  $I > II > III > IV$       (B)  $IV > III > II > I$       (C)  $III > II > I > IV$       (D)  $I > IV > II > III$

Q.2 In the given reaction



[X] will be :

- (A)  $\text{HCHO}$       (B)  $\begin{array}{c} \text{CH}_2\text{-OH} \\ | \\ \text{CH}_2\text{-OH} \end{array} + \text{H}^{\oplus}$       (C)  $\begin{array}{c} \text{CH}_2\text{-OH} \\ | \\ \text{CH}_2\text{-OH} \end{array} + \overset{\ominus}{\text{OH}}$       (D)  $\text{HCN}$

Q.3 In the given reaction:  $\text{C}_6\text{H}_5-\text{C}-\text{H} \xrightarrow{\text{NH}_2\text{OH}/\text{H}^+} [\text{X}]$

[X] will be:

- (A) Only syn oxime  
(B) Only anti oxime  
(C) Mixture of syn and anti oxime  
(D) Secondary amide

Q.4 Acetophenone can be obtained by the distillation of :

- (A)  $(\text{C}_6\text{H}_5\text{COO})_2\text{Ca}$  (B)  $(\text{CH}_3\text{COO})_2\text{Ca}$   
(C)  $(\text{C}_6\text{H}_5\text{COO})_2\text{Ca}$  and  $(\text{CH}_3\text{COO})_2\text{Ca}$  (D)  $(\text{C}_6\text{H}_5\text{COO})_2\text{Ca}$  and  $(\text{HCOO})_2\text{Ca}$

Q.5 Gem dihalide on hydrolysis gives :

- (A) Vic diol                      (B) Gem diol                      (C) Carbonyl compound                      (D) Carboxylic acid

Q.6 Acetal or ketal is:

- (A) Vic dialkoxy compound                      (B)  $\alpha$ ,  $\omega$ -dialkoxy compound  
(C)  $\alpha$ -alkoxy alcohol                          (D) Gem dialkoxy compound

Q.7 Cross cannizzaro reaction is example of:

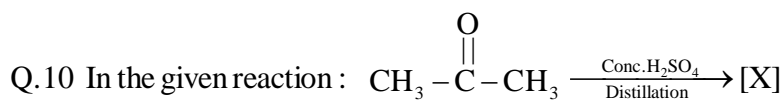
- (A) Redox reaction      (B) Disproportionation      (C) Both (A) and (B)      (D) Only oxidation

Q.8 Acetaldehyde can be converted into  $\text{HOCH}_2 - \text{C}(\text{CH}_2\text{OH})_2$  by which reagent ?

- (A) KOH  
(B) KOH followed by LAH  
(C) excess of HCHO and KOH  
(D) KCN followed by SBH

Q.9 Which one of the combinations will give propanaldehyde on dry distillation ?

- (A)  $(\text{C}_6\text{H}_5\text{COO})_2\text{Ca}$  and  $(\text{HCOO})_2\text{Ca}$  (B)  $(\text{CH}_3\text{COO})_2\text{Ca}$  and  $(\text{CH}_3\text{CH}_2\text{COO})_2\text{Ca}$   
(C)  $(\text{CH}_3\text{CH}_2\text{COO})_2\text{Ca}$  and  $(\text{HCOO})_2\text{Ca}$  (D)  $(\text{CH}_3\text{COO})_2\text{Ca}$  and  $(\text{CH}_3\text{COO})_2\text{Ca}$



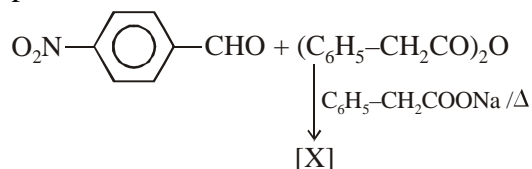
[X] will be :

- (A) Methyl oxide (B) Phorone  
(C) 1, 3, 5-Trimethylbenzene (D) 2-Butyne

Q.11 Grignard reagents can not give carbonyl compounds with :

- (A)  $\text{CO}_2$  (B)  $\text{RCOCl}$  (C)  $\text{RCN}$  (D)  $\text{RCOOR}$

Q.12 The product of the reaction :



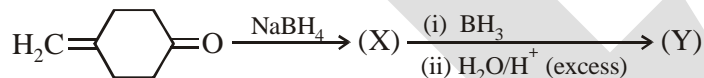
will be :

- (A)  $\text{C}_6\text{H}_5-\text{CH}=\text{CH}-\text{COOH}$  (B)  $\text{NO}_2-\text{C}_6\text{H}_4-\text{CH}=\text{CH}-\text{COOH}$   
(C)  $\text{C}_6\text{H}_5-\text{CH}=\underset{\text{CH}_3}{\text{C}}-\text{COOH}$  (D)  $\text{NO}_2-\text{C}_6\text{H}_4-\text{CH}=\underset{\text{C}_6\text{H}_5}{\text{C}}-\text{COOH}$

Q.13 Cyanohydrin of which compound on hydrolysis will give lactic acid ?

- (A)  $\text{C}_6\text{H}_5\text{CHO}$  (B)  $\text{HCHO}$  (C)  $\text{CH}_3\text{CHO}$  (D)  $\text{CH}_3-\text{CH}_2-\text{CHO}$

Q.14 In the given reaction :

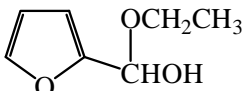
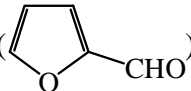


(X) and (Y) are :

- (A)  $\text{CH}_2=\text{C}_6\text{H}_{10}-\text{OH}$  and  $\text{HOCH}_2-\text{C}_6\text{H}_{10}=\text{O}$   
(B)  $\text{CH}_3-\text{C}_6\text{H}_{10}=\text{O}$  and  $\text{HOCH}_2-\text{C}_6\text{H}_{10}=\text{O}$   
(C)  $\text{CH}_2=\text{C}_6\text{H}_{10}-\text{OH}$  and  $\text{CH}_3-\text{C}_6\text{H}_{10}-\text{OH}$   
(D)  $\text{CH}_2-\text{C}_6\text{H}_{10}-\text{OH}$  and  $\text{CH}_3-\text{C}_6\text{H}_{10}(\text{OH})=\text{O}$

Q.15 Acetaldehyde cannot give :

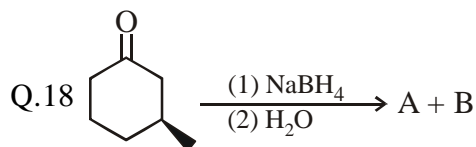
- (A) Iodoform test (B) Lucas test (C) Benedict test (D) Tollens test

Q.16 Compound  formed by the reaction of furfural () with ethanol is :

- (A) an aldol (B) an acetal (C) a ketal (D) a hemiacetal

Q.17 A compound with molecular formula  $C_8H_{18}O_4$  does not give litmus test and does not give colour with 2,4-DNP. It reacts with excess  $MeCOCl$  to give a compound whose vapour density is 152. Compound A contains how many hydroxy groups ?

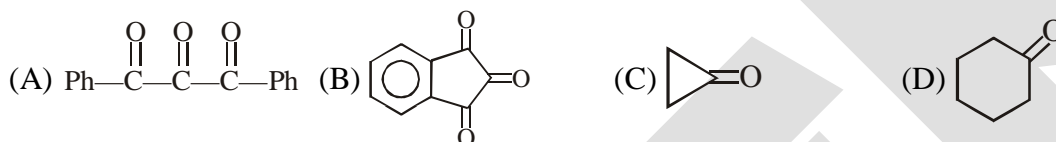
- (A) 1 (B) 2 (C) 3 (D) 4



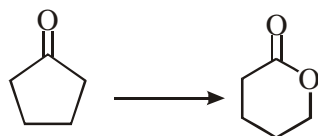
Identify relationship between A & B products ?

- (A) Diastereoisomers (B) Enantiomers (C) Positional isomer (D) Identical

Q.19 Which of the following does not form a stable hydrate by the addition of  $H_2O$ ?

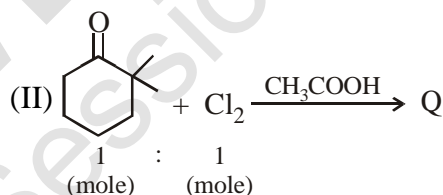
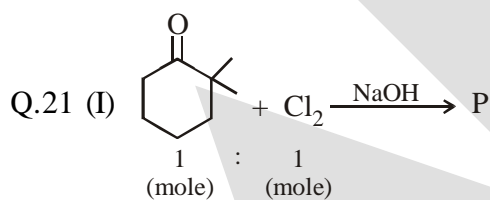
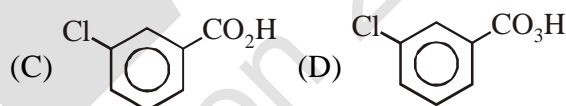


Q.20 The conversion

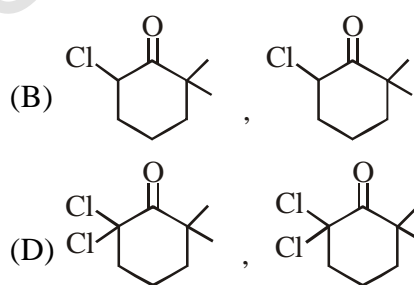
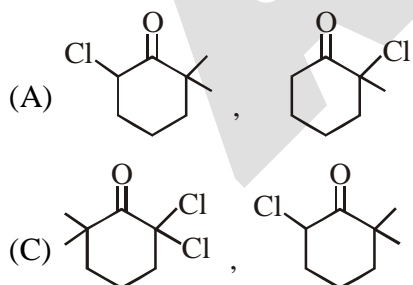


can be effected by using the reagent

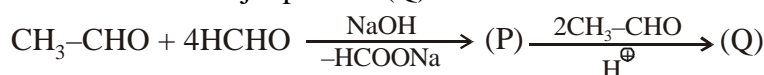
- (A) Tollen's reagent (B)  $O_3$



Organic product P & Q are respectively -

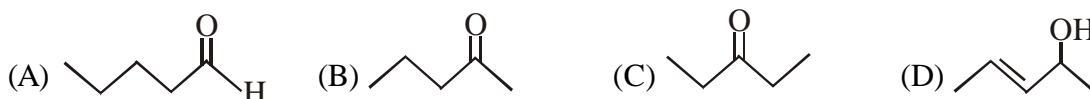


Q.22 Total number of stereoisomers of major product (Q) are :

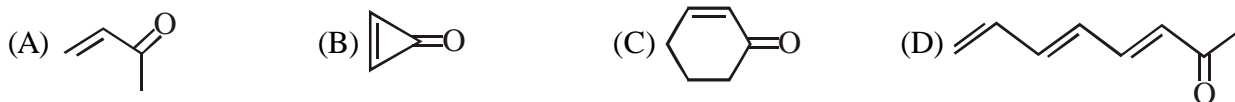


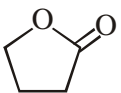
- (A) 0 (B) 4 (C) 8 (D) 2

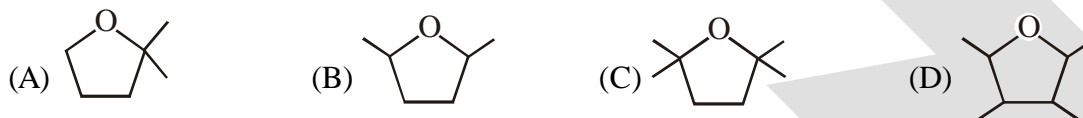
Q.23 An organic compound (A),  $C_5H_{10}O$ , reacts with hydrazine to form a hydrazone derivative (B). The hydrazone (B) on being heated with KOH at about  $180^\circ C$ , gives n-pentane. The compound (A) does not respond positively to Tollen's reagent and to the iodoform test. The compound (A) is



Q.24 The compound having the highest dipole moment is :



Q.25   $\xrightarrow[(2) H_2O]{(1) \text{ Excess MeMgCl}}$  (A)  $\xrightarrow[H_2SO_4]{\text{conc.}}$  'B' Identify 'B' product ?



**Question No. 26 to 28 (3 questions)**

An alkene (A)  $C_{16}H_{16}$  on ozonolysis gives only product (B)  $C_8H_8O$ . (B) also can be obtained by hydrolysis of the product obtained by reaction between cyano benzene and  $CH_3MgBr$ . (A) can show geometrical isomerism and it can decolourise  $Br_2$  water. (B) on treatment with  $SeO_2$  produces (C)

Q.26 Which is not correct about (A) ?

- (A) A is optically inactive  
(B) On catalytic hydrogenation 'trans' form of A produces racemic mixture  
(C) A can be prepared by Wittig reaction on acetophenone with  $Ph_3P=C(CH_3)Ph$ .  
(D) On treatment with per acid followed by hydrolysis 'trans' form of A produces racemic mixture

Q.27 Which is not correct about B ?

- (A) It gives iodoform test  
(B) On treatment with  $LiAlH_4$ ,  $H_2O$  it produces a compound which also responds to iodoform test.  
(C) It gives Tollen's test  
(D) On treatment with  $NH_2NH_2$  followed by alc. KOH at high temperature, it produces ethyl benzene

Q.28 Which is not correct about C?

- (A) On treatment with  $NaBH_4$  it will produce a diol.  
(B) On treatment with  $OH^-$  (conc.) followed by acidification racemic mixture of a carboxylic acid is obtained  
(C) It gives Tollen's test  
(D) It can take part in aldol condensation

**(Question No. 29 & 30)**

Questions given below consist of two statements each printed as Assertion (A) and Reason (R); while answering these questions you are required to choose any one of the following four responses:

- (A) If both (A) and (R) are true and (R) is the correct explanation of (A)  
(B) If both (A) and (R) are true but (R) is not correct explanation of (A)  
(C) If (A) is true but (R) is false  
(D) If (A) is false and (R) is true

Q.29 **Assertion** : Benzaldehyde with HCN gives two isomeric compounds

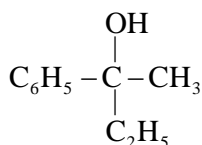
**Reason** : Both nitrile and isonitrile compounds are possible when HCN reacts with carbonyl group.

Q.30 **Assertion** :  $Cl_3C-C(=O)H \xrightarrow{NaOH} Cl_3C-CH_2OH + Cl_3C-COONa$

**Reason** : There are no  $\alpha-H$  in this compound, so it can't give aldol.

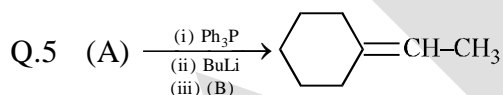
EXERCISE # II

- Q.1 Two isomeric ketones, 3-pentanone and 2-pentanone can be distinguished by :  
 (A)  $I_2 / NaOH$  (B)  $NaSO_3H$  (C)  $NaCN / HCl$  (D) 2,4-DNP
- Q.2 An optically inactive alcohol (A)  $C_6H_{12}O$  is oxidized by  $MnO_2$  to produce optically inactive carbonyl compound while reduction of (A) by  $H_2/Ni$  produces optically active compound. Possible structure(s) of alcohol is/are  
 (A) Hex-2-ene-1-ol (B) Hex-3-ene-2-ol  
 (C) 2-Methyl pent-2-ene-1-ol (D) 3-Methyl pent-2-ene-1-ol
- Q.3 Consider the structure of given alcohol:

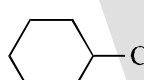
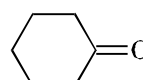



This alcohol can be prepared from:

- (A)  $C_6H_5 - \overset{O}{\parallel} C - CH_3$  and  $C_2H_5MgBr$  (B)  $CH_3 - CH_2 - \overset{O}{\parallel} C - CH_3$  and  $C_6H_5MgBr$   
 (C)  $C_6H_5 - \overset{O}{\parallel} C - C_2H_5$  and  $CH_3MgBr$  (D)  $C_6H_5 - \overset{O}{\parallel} C - Cl$  and  $C_2H_5MgCl$
- Q.4 Which of the following compounds will not give aldol condensation :  
 (A) Acetaldehyde (B) Formaldehyde (C) Pivaldehyde (D) Crotonaldehyde



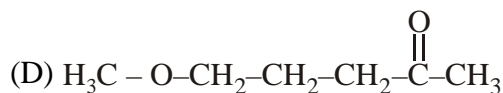
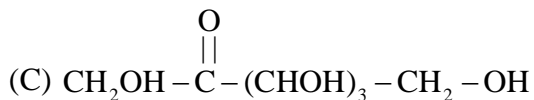
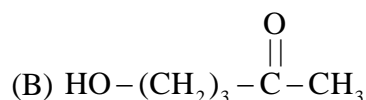
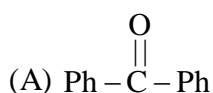
In above reaction (A) and (B) will respectively be

- (A)  &  $CH_3CHO$  (B)  $CH_3CH_2Cl$  &   
 (C)  &  $HCHO$  (D)  $Cl - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - Cl$  &  $CH_3CHO$

- Q.6 Stability of hydrates of carbonyl compounds depends on:  
 (A) Steric hindrance (B) Presence of  $-I$  group on gemdiol carbon  
 (C) Intramolecular hydrogen bonding (D) angle strain in carbonyl compound
- Q.7 Which of the following can be used for protection of carbonyl group  
 (A)  $CH_2OH - CH_2OH / H^+$  (B)  $CH_2OH - CH_2 - CH_2OH / H^+$   
 (C)  $HS - (CH_2)_3 - SH$  (D)  $CH_2OH - CH_2 - CHO$



Q.8 Which of the following(s) will form stable hemiketal :



Q.9 Mixture of  $\text{Ph}-\text{CHO}$  &  $\text{HCHO}$  is treated with  $\text{NaOH}$  then Cannizzaro reaction involves:

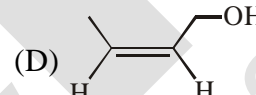
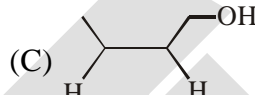
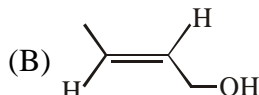
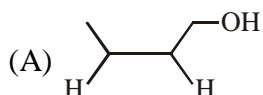
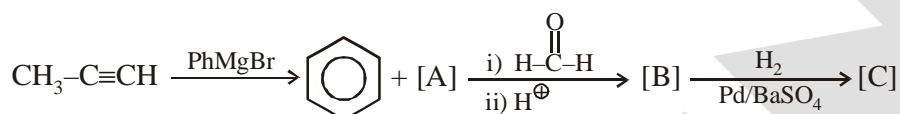
(A) Oxidation of  $\text{HCHO}$

(B) Reduction of  $\text{HCHO}$

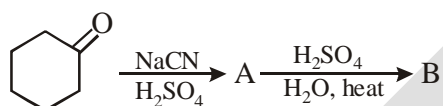
(C) Oxidation of  $\text{Ph}-\text{CHO}$

(D) Reduction of  $\text{Ph}-\text{CHO}$

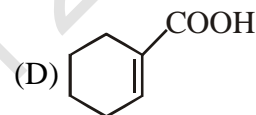
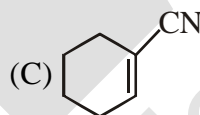
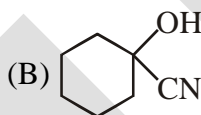
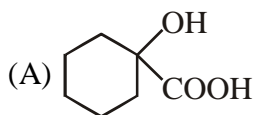
Q.10 Final product in the given reaction sequence is :



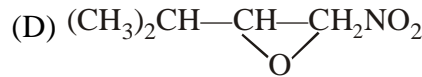
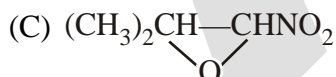
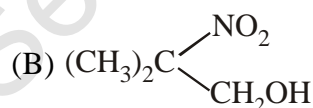
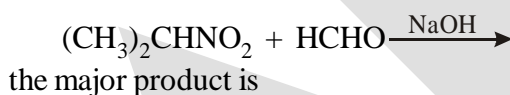
Q.11 Consider the following sequence of reactions.



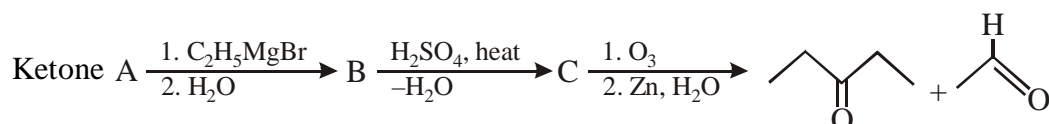
The major product (B) is :



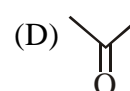
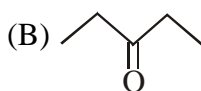
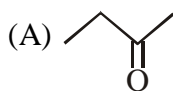
Q.12 In the reaction



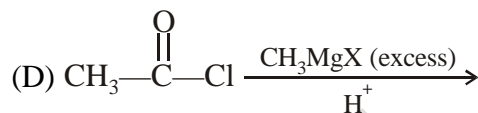
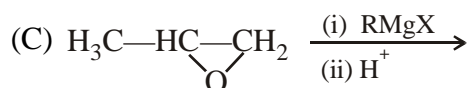
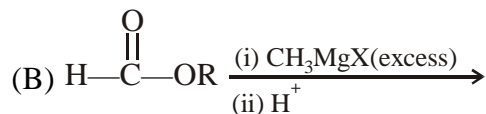
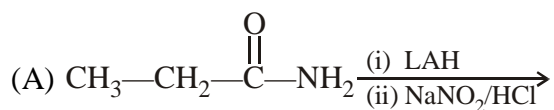
Q.13 Consider the following sequence of reactions.



The ketone (A) is :

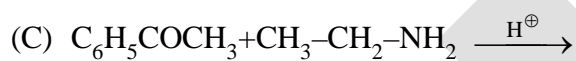
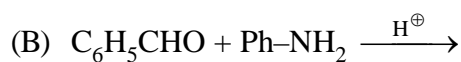
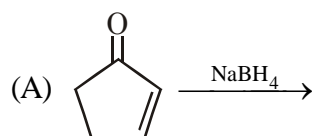


Q.14 Which of the following reactions will give(s) 2° alcohol as a major product :



Q.15 Match list-I with list-II :

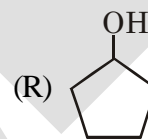
List - I



List - II

(P) Acetal

(Q) Schiff's base

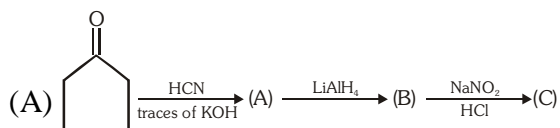


(S) Imine

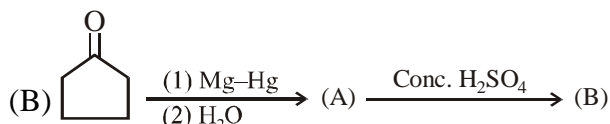
## EXERCISE # III

## Q.1 Column - I

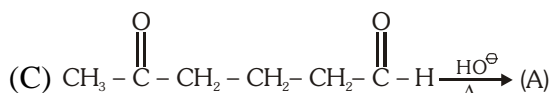
## Column - II



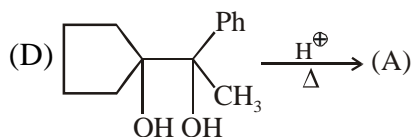
(P) Formation of six member ring takes place



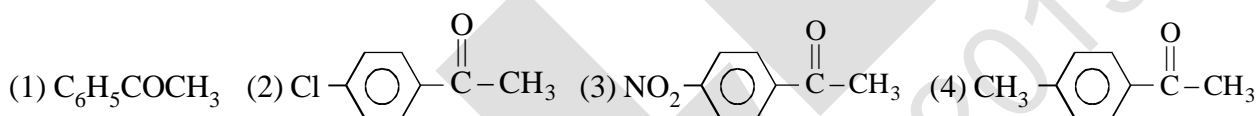
(Q) Final product is Ketone



(R) Final product formed will give positive Iodoform test

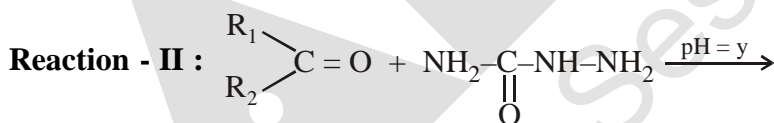
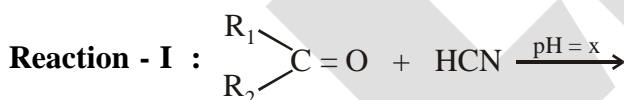


(S) Final product formed will react with 2,4-DNP. (2,4-Di-nitrophenyl hydrazine)

Q.2 Arrange the following compounds in decreasing order of  $K_{\text{eq}}$  for hydrate formation.

## Paragraph for Q. 03 to 04

Two reactions which are example of nucleophilic attack are given as below .



Q.3 Value of x is :

(A)  $x \leq 4.5$ (B)  $x = 6$ (C)  $x > 7$ 

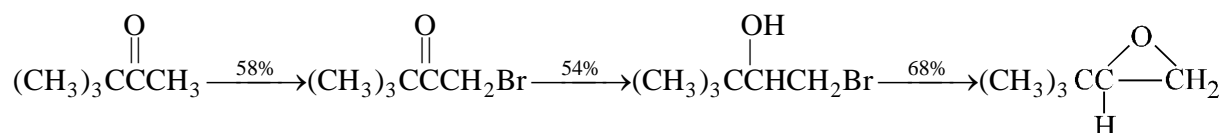
(D) Can't decide

Q.4 Value of y is :

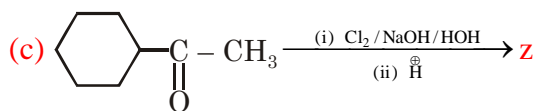
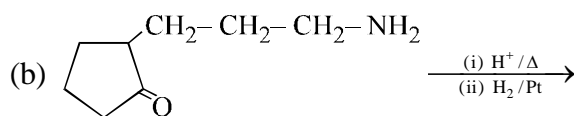
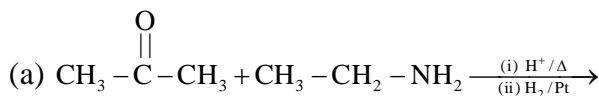
(A)  $x = 4.5$ (B)  $x = 1.5$ (C)  $x = 7$ (D)  $x = 9$ 

Q.5 Some Grignard reagents react with ethyl orthoformate, followed by acidic hydrolysis, to give aldehydes. Propose mechanisms for the two steps in this synthesis.

Q.6 A synthesis that begins with 3,3-dimethyl-2-butanone gives the epoxide shown. Suggest reagents appropriate for each step in the synthesis.

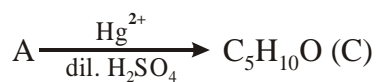
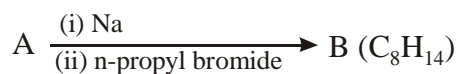


Q.7 Predict the organic products :

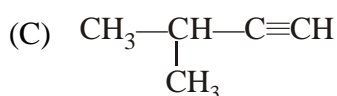
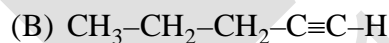


Paragraph for Q.No.8 to 9

A(Hydrocarbon) ( $\text{C} \Rightarrow 88.24\%$ ) [Molecular weight of A = 68]



Q.8 'A' can be :



Q.9 Correct statement regarding C is.

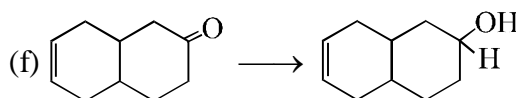
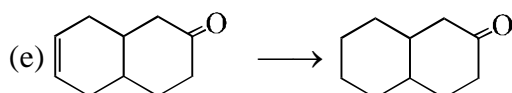
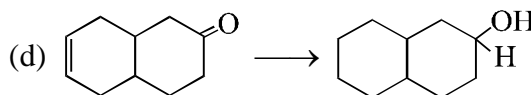
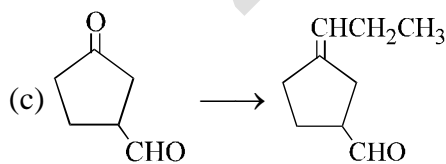
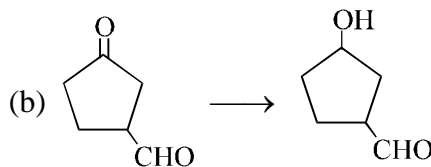
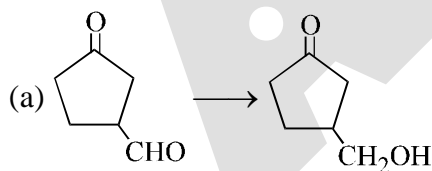
(A) C reacts with fehling solution to give red ppt.

(B) C gives +ve iodoform test

(C) C give -ve 2, 4, D.N.P test

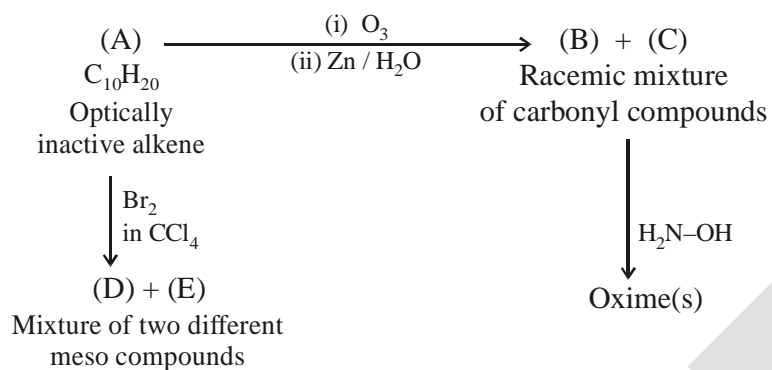
(D) C is aldehyde

Q.10 Show how you would accomplish the following syntheses efficiently and in good yield. You may use any necessary reagents.

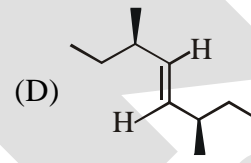
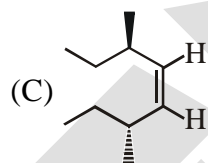
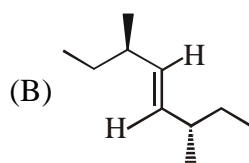
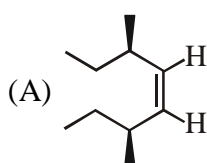


## Paragraph for Q.No. 11 to 12

In given reaction sequence



11. Alkene A is :



12. How many total oxime(s) is/are obtained

(A) 1

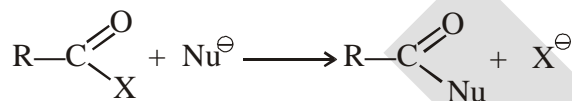
(B) 2

(C) 3


(D) 4

### EXERCISE # IV (MAINS)

- Q.1 When  $\text{CH}_2 = \text{CH}-\text{COOH}$  is reduced with  $\text{LiAlH}_4$ , the compound obtained will be -  
 (1)  $\text{CH}_3-\text{CH}_2-\text{CH}_2\text{OH}$  (2)  $\text{CH}_3-\text{CH}_2-\text{CHO}$  [AIEEE-2003]  
 (3)  $\text{CH}_3-\text{CH}_2-\text{COOH}$  (4)  $\text{CH}_2=\text{CH}-\text{CH}_2\text{OH}$
- Q.2 Which one of the following undergoes reaction with 50% sodium hydroxide solution to give the corresponding alcohol and acid ? [AIEEE-2004]  
 (1) Phenol (2) Benzaldehyde (3) Butanal (4) Benzoic acid
- Q.3 Which one of the following is reduced with  $\text{Zn-Hg/HCl}$  to give the corresponding hydrocarbon [AIEEE-2004]  
 (1) Butan-2-one (2) Acetic acid (3) Acetamide (4) Ethyl acetate
- Q.4 On mixing ethyl acetate with aqueous sodium chloride, the composition of the resultant solution is  
 (1)  $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaCl}$  (2)  $\text{CH}_3\text{COONa} + \text{C}_2\text{H}_5\text{OH}$  [AIEEE-2004]  
 (3)  $\text{CH}_3\text{COCl} + \text{C}_2\text{H}_5\text{OH} + \text{NaOH}$  (4)  $\text{CH}_3\text{Cl} + \text{C}_2\text{H}_5\text{COONa}$
- Q.5 The best reagent to convert pent-3-en-2-ol into pent-3-en-2-one is - [AIEEE-2005]  
 (1) Acidic dichromate (2) Acidic permanganate  
 (3) Pyridinium chloro-chromate (4) Chromic anhydride in glacial acetic acid
- Q.6 Rate of the reaction- [AIEEE-2005]



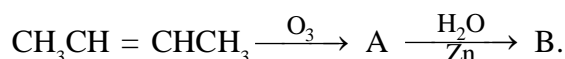
is fastest when X is -

- Q.7 Among the following the one that gives positive iodoform test upon reaction with  $I_2$  and  $NaOH$  is-
- (1)  $CH_3CH_2CH(OH)CH_2CH_3$  (2)  $C_6H_5CH_2CH_2OH$  [AIEEE-2006]
- (3)  (4)  $PhCHOHCH_3$

Q.8 In the following sequence of reactions



- (1) Butanal (2) n-Butyl alcohol  
(3) n-Propyl alcohol (4) Propanal
- Q.9 In the following sequence of reactions, the alkene affords the compound 'B' :- **[AIEEE-2008]**



The compound B is

- (1)  $\text{CH}_3\text{CH}_2\text{CHO}$       (2)  $\text{CH}_3\text{COCH}_3$       (3)  $\text{CH}_3\text{CH}_2\text{COCH}_3$       (4)  $\text{CH}_3\text{CHO}$   
Q.10 Bakelite is obtained from phenol by reacting with **[AIEEE-2008]**  
(1)  $(\text{CH}_2\text{OH})_2$       (2)  $\text{CH}_3\text{CHO}$       (3)  $\text{CH}_3\text{COCH}_3$       (4)  $\text{HCHO}$

Q.11 Which of the following on heating with aqueous KOH, produces acetaldehyde ? [AIEEE-2009]

- (1)  $\text{CH}_2\text{ClCH}_2\text{Cl}$  (2)  $\text{CH}_3\text{CHCl}_2$  (3)  $\text{CH}_3\text{COCl}$  (4)  $\text{CH}_3\text{CH}_2\text{Cl}$

Q.12 In Cannizzaro reaction given below :-

[AIEEE-2009]



the slowest step is :-

- (1) The abstraction of proton from the carboxylic group  
 (2) The deprotonation of  $\text{PhCH}_2\text{OH}$   
 (3) The attack of  $:\ddot{\text{O}}\text{H}^-$  at the carboxyl group  
 (4) The transfer of hydride to the carbonyl group

Q.13 One mole of a symmetrical alkene on ozonolysis gives two moles of an aldehyde having a molecular mass of 44 u. The alkene is :-

[AIEEE-2010]

- (1) Ethene (2) Propene (3) 1-Butene (4) 2-Butene

Q.14 Ozonolysis of an organic compound gives formaldehyde as one of the products. This confirms the presence of :-

[AIEEE-2011]

- (1) An isopropyl group (2) An acetylenic triple bond  
 (3) Two ethylenic double bonds (4) A vinyl group

Q.15 Ozonolysis of an organic compound 'A' produces acetone and propionaldehyde in equimolar mixture. Identify 'A' from the following compounds :-

[AIEEE-2011]

- (1) 2-Methyl - 1- pentene (2) 1-Pentene  
 (3) 2-Pentene (4) 2-Methyl-2-pentene

Q.16 Trichloroacetaldehyde was subjected to assumed Cannizzaro's reaction by using NaOH. The mixture of the products contains sodium trichloroacetate and another compound. The other compound is :-

[AIEEE-2011]

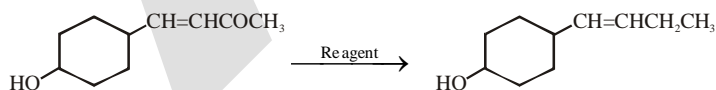
- (1) 2,2,2-Trichloropropanol (2) Chloroform  
 (3) 2,2,2-Trichloroethanol (4) Trichloromethanol

Q.17 Silver Mirror test is given by which one of the following compounds?

[AIEEE-2011]

- (1) Formaldehyde (2) Benzophenone (3) Acetaldehyde (4) Acetone

Q.18 In the given transformation, which of the following is the most appropriate reagent ? [AIEEE-2012]



- (1)  $\text{NaBH}_4$  (2)  $\text{NH}_2\text{NH}_2, \text{OH}^-$  (3)  $\text{Zn} - \text{Hg} / \text{HCl}$  (4)  $\text{Na}, \text{Liq. NH}_3$

Q.19 Iodoform can be prepared from all except :-

[AIEEE-2012]

- (1) Isobutyl alcohol (2) Ethyl methyl ketone  
 (3) Isopropyl alcohol (4) 3-Methyl-2-butanone

Q.20 A compound with molecular mass 180 is acylated with  $\text{CH}_3\text{COCl}$  to get a compound with molecular mass 390. The number of amino groups present per molecule of the former compound is :-

- (1) 2 (2) 5 (3) 4 (4) 6 [JEE(Main)-2013]

Q.21 The major organic compound formed by the reaction of 1, 1, 1-trichloroethane with silver powder is :-

[JEE(Main)-2014]

- (1) 2-Butyne (2) 2-Butene (3) Acetylene (4) Ethene

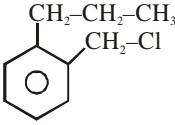
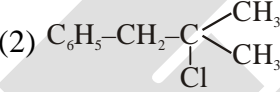
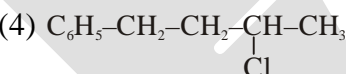
Q.22 The most suitable reagent for the conversion of  $R-CH_2-OH \rightarrow R-CHO$  is :-

[JEE(Main)-2014]

- (1)  $CrO_3$  (2) PCC (Pyridinium chlorochromate)  
(3)  $KMnO_4$  (4)  $K_2Cr_2O_7$

Q.23 A compound A with molecular formula  $C_{10}H_{13}Cl$  gives a white precipitate on adding silver nitrate solution. A on reacting with alcoholic KOH gives compound B as the main product. B on ozonolysis gives C and D. C gives Cannizzaro reaction but not aldol condensation. D gives aldol condensation but not Cannizzaro reaction. A is :

[JEE(Main)-2015]

- (1)  (2)   
(3)  $C_6H_5-CH_2-CH_2-CH_2-CH_2-Cl$  (4) 

Q.24 In the reaction sequence

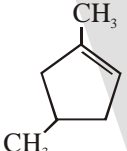
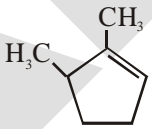
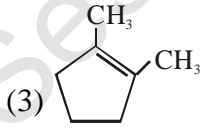
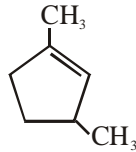
[JEE(Main)-2015]

$2CH_3CHO \xrightarrow{OH^-} A \xrightarrow{\Delta} B$ ; the product B is:-

- (1)  $CH_3-CH=CH-CHO$  (2)  $CH_3-CH_2-CH_2-CH_3$   
(3)  $CH_3-CH_2-CH_2-CH_2-OH$  (4) 

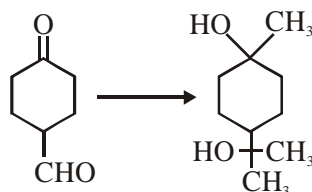
Q.25 Which compound would give 5-keto-2-methyl hexanal upon ozonolysis?

[JEE(Main) 2015]

- (1)  (2)  (3)  (4) 

Q.26 The correct sequence of reagents for the following conversion will be :-

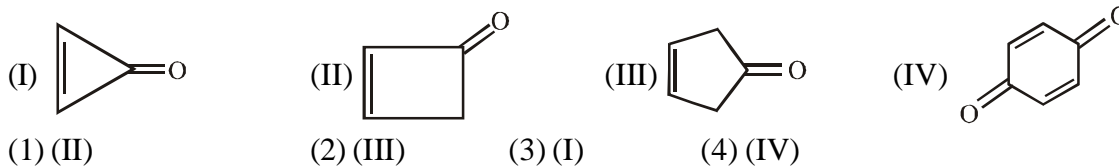
[JEE(Main)-2017]



- (1)  $[Ag(NH_3)_2]^+ OH^-$ ,  $H^+/CH_3OH$ ,  $CH_3MgBr$   
(2)  $CH_3MgBr$ ,  $H^+/CH_3OH$ ,  $[Ag(NH_3)_2]^+ OH^-$   
(3)  $CH_3MgBr$ ,  $[Ag(NH_3)_2]^+ OH^-$ ,  $H^+/CH_3OH$   
(4)  $[Ag(NH_3)_2]^+ OH^-$ ,  $CH_3MgBr$ ,  $H^+/CH_3OH$



Q.27 Which of the following compounds will show highest dipole moment ? [JEE(Main-on-line)-2017]



Q.28 Glucose on prolonged heating with HI gives :

[JEE(Main)-2018]

- (1) 1-Hexene (2) Hexanoic acid (3) 6-iodohexanal (4) n-Hexane

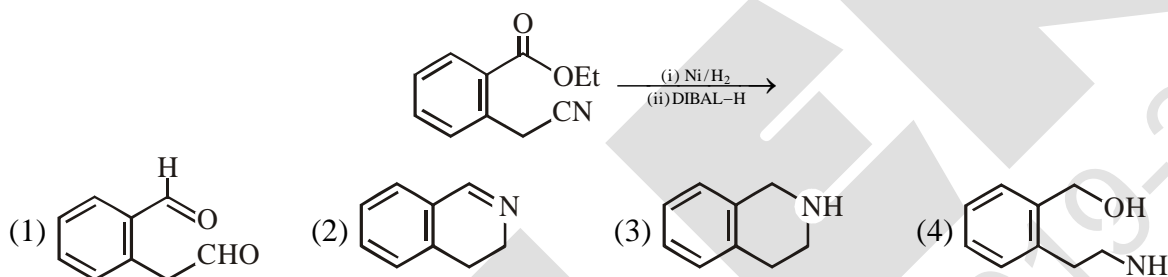
Q.29 Which of the following compounds will most readily be dehydrated to give alkene under acidic condition?

[JEE(Main-on-line)-2018]

- (1) 4-Hydroxypentan-2-one (2) 2-Hydroxycyclopentanone  
(3) 3-Hydroxypentan-2-one (4) 1-Pentanol

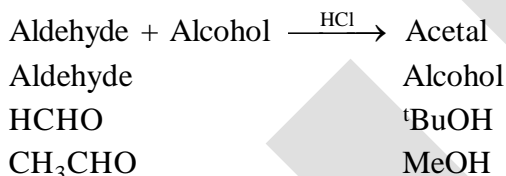
Q.30. The major product of the following reaction is:

[JEE-Main(January)-2019]



Q.31 In the following reaction

[JEE-Main(January)-2019]

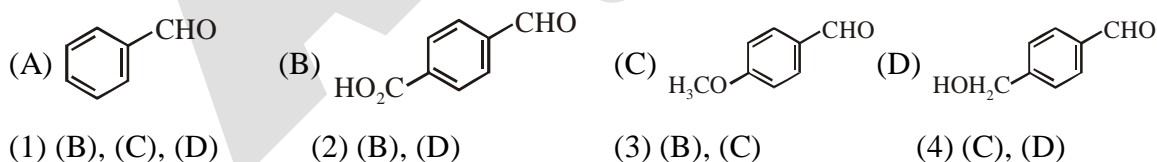


The best combinations is :

- (1) HCHO and MeOH (2) HCHO and <sup>t</sup>BuOH  
(3) CH<sub>3</sub>CHO and MeOH (4) CH<sub>3</sub>CHO and <sup>t</sup>BuOH

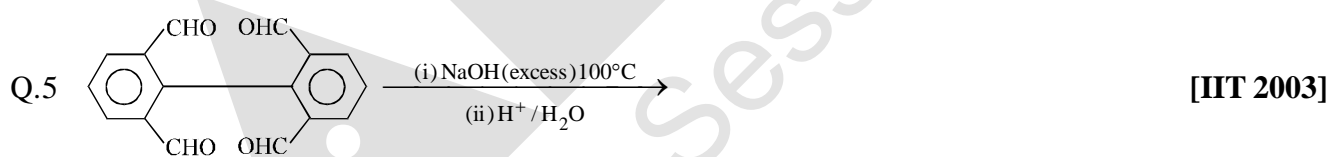
Q.32 The aldehydes which will not form Grignard product with one equivalent Grignard reagents are :

[JEE-Main(January)-2019]

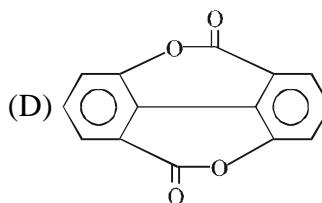
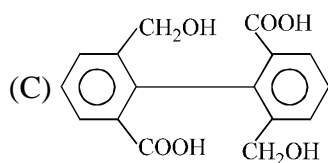
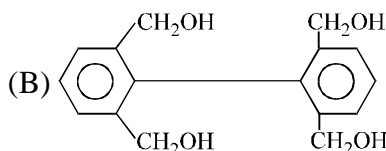
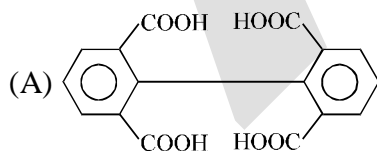


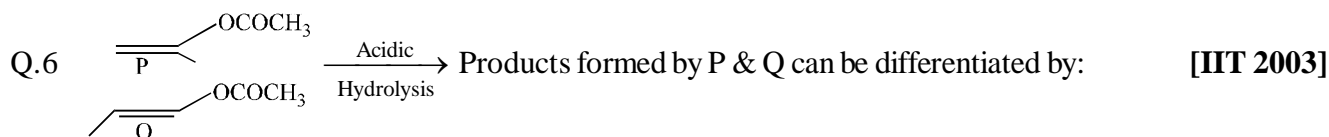
**EXERCISE-IV # (A) (OBJECTIVE QUESTIONS)**

- Q.1 Which of the following has the most acidic hydrogen: [IIT 2000]
- (A) 3-hexanone (B) 2,4-hexanedione  
(C) 2,5-hexanedione (D) 2,3-hexandione
- Q.2 A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH solution gives:
- (A) benzyl alcohol and sodium formate (B) sodium benzoate and methyl alcohol  
(C) sodium benzoate and sodium formate (D) benzyl alcohol and methyl alcohol [IIT 2001]
- Q.3 1-propanol & 2-propanol can be best distinguished by : [IIT 2001]
- (A) Oxidation with alkaline  $\text{KMnO}_4$  followed by reaction with Fehling solution  
(B) Oxidation with acidic dichromate followed by reaction with Fehling solution  
(C) Oxidation by heating with copper followed by reaction with Fehling solution  
(D) Oxidation with concentrated  $\text{H}_2\text{SO}_4$  followed by reaction with Fehling solution
- Q.4 Compound A (molecular formula  $\text{C}_3\text{H}_8\text{O}$ ) is treated with acidified potassium dichromate to form a product B (molecular formula  $\text{C}_3\text{H}_6\text{O}$ ). B forms a shining silver mirror on warming with ammonical silver nitrate. B when treated with an aqueous solution of  $\text{H}_2\text{NCONHNH}_2$ ,  $\text{HCl}$  and sodium acetate gives a product C. Identify the structure of C. [IIT 2002]
- (A)  $\text{CH}_3\text{CH}_2\text{CH} = \text{NNHCONH}_2$  (B)  $\text{CH}_3 - \underset{\text{CH}_3}{\text{C}} = \text{NNHCONH}_2$   
(C)  $\text{CH}_3 - \text{C} = \text{NCONHNH}_2$  (D)  $\text{CH}_3\text{CH}_2\text{CH} = \text{NCONHNH}_2$



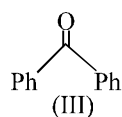
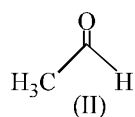
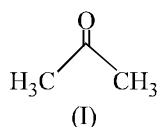
any one of the products formed is :



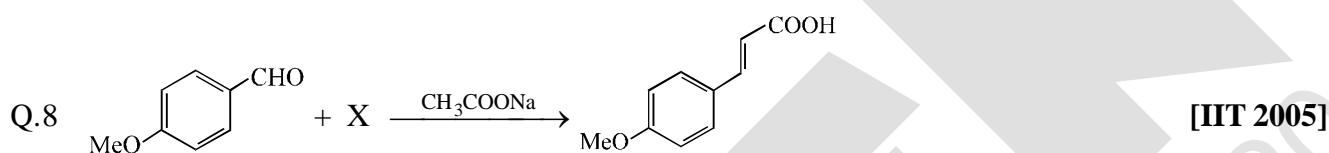


- (A) 2, 4 DNP (B) Lucas reagent ( $\text{ZnCl}_2$ ) conc. HCl  
(C)  $\text{NaHSO}_3$  (D) Fehlings solution

Q.7 The order of reactivity of phenyl Magnesium Bromide with the following compounds is [IIT 2004]



- (A)  $\text{II} > \text{III} > \text{I}$  (B)  $\text{I} > \text{III} > \text{II}$  (C)  $\text{II} > \text{I} > \text{III}$  (D) All react with the same rate



What is X?

- (A)  $\text{CH}_3\text{COOH}$  (B)  $\text{BrCH}_2\text{COOH}$  (C)  $(\text{CH}_3\text{CO})_2\text{O}$  (D)  $\text{CHO}-\text{COOH}$

Q.9 The smallest ketone and its next homologue are reacted with  $\text{NH}_2\text{OH}$  to form oxime.

- (A) Two different oximes are formed (B) Three different oximes are formed  
(C) Two oximes are optically active (D) All oximes are optically active [IIT 2006]

Q.10 Cyclohexene on ozonolysis followed by reaction with zinc dust and water gives compound E. Compound E on further treatment with aqueous KOH yields compound F. Compound F is



Q.11 **Statement-1** : Glucose gives a reddish-brown precipitate with Fehling's solution.

*because*

**Statement-2** : Reaction of glucose with Fehling's solution gives  $\text{CuO}$  and gluconic acid.

- (A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.  
(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.  
(C) Statement-1 is True, Statement-2 is False.  
(D) Statement-1 is False, Statement-2 is True.

[IIT-JEE(ADV.)- 2007]

Q.12 Match the compounds/ion in column I with their properties/ reaction in Column II. Indicate your answer by darkening the appropriate bubbles of the  $4 \times 4$  matrix given in the ORS.

[IIT-JEE(ADV.)- 2007]

**Column I**

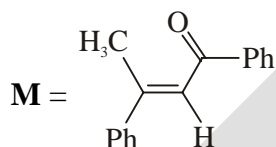
- (A)  $C_6H_5CHO$   
(B)  $CH_3C \equiv CH$   
(C)  $CN^-$   
(D)  $I^-$

**Column II**

- (P) gives precipitate with 2,4-dinitrophenylhydrazine  
(Q) gives precipitate with  $AgNO_3$   
(R) is a nucleophile  
(S) is involved in cyanohydrin formation

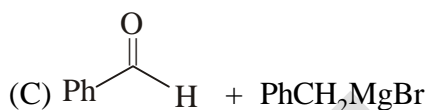
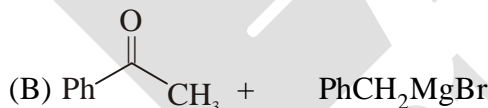
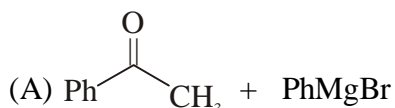
**Paragraph for Question No. 13 to 15**

A tertiary alcohol **H** upon acid catalysed dehydration gives a product **I**. Ozonolysis of **I** leads to compounds **J** and **K**. Compound **J** upon reaction with KOH gives benzyl alcohol and a compound **L**, whereas **K** on reaction with KOH gives only **M**.



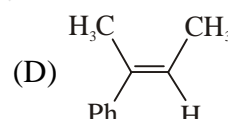
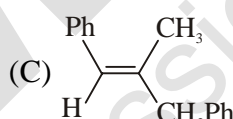
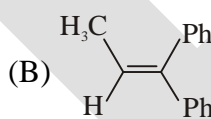
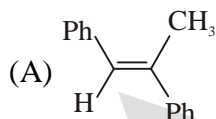
Q.13 Compound **H** is formed by the reaction of

[IIT-JEE(ADV.)- 2008]



Q.14 The structure of compound **I** is

[IIT-JEE(ADV.)- 2008]



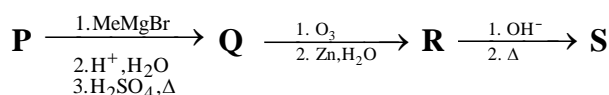
Q.15 The structures of compounds **J**, **K** and **L**, respectively, are

[IIT-JEE(ADV.)- 2008]

- (A)  $PhCOCH_3$ ,  $PhCH_2COCH_3$  and  $PhCH_2COO^-K^+$   
(B)  $PhCHO$ ,  $PhCH_2CHO$  and  $PhCOO^-K^+$   
(C)  $PhCOCH_3$ ,  $PhCH_2CHO$  and  $CH_3COO^-K^+$   
(D)  $PhCHO$ ,  $PhCOCH_3$  and  $PhCOO^-K^+$

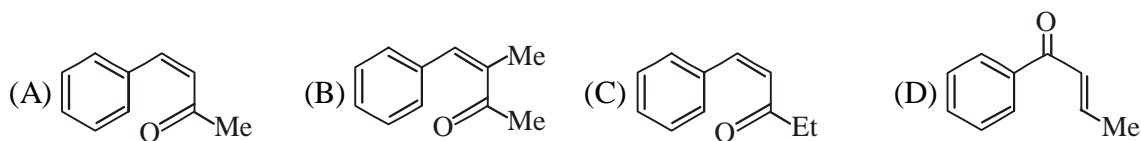
**Paragraph for Question Nos. 16 to 38**

A carbonyl compound **P**, which gives positive iodoform test, undergoes reaction with  $MeMgBr$  followed by dehydration to give an olefin **Q**. Ozonolysis of **Q** leads to a dicarbonyl compound **R**, which undergoes intramolecular aldol reaction to give predominantly **S**.

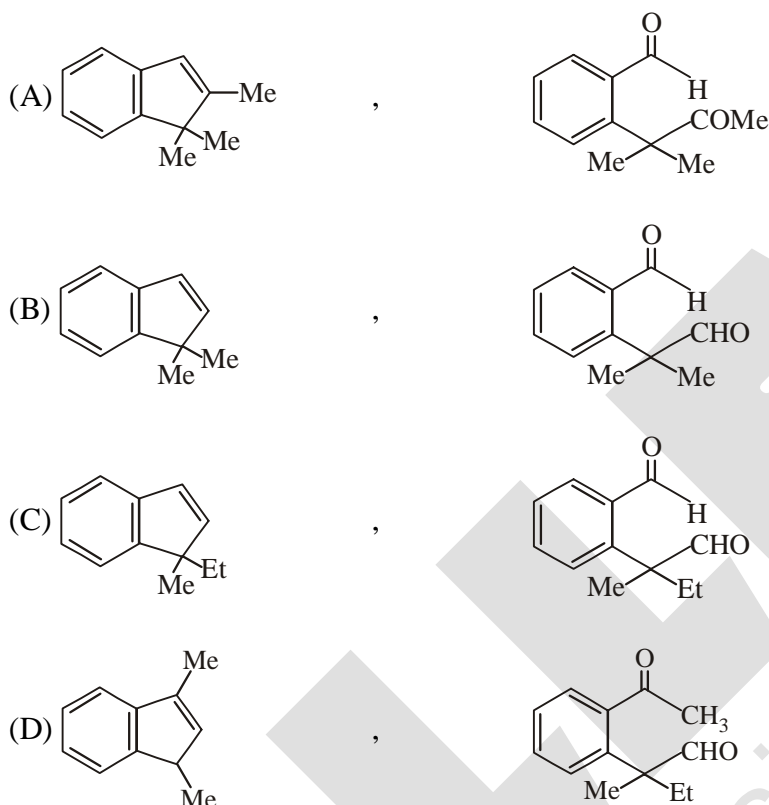


Q.16 The structure of the carbonyl compound **P** is

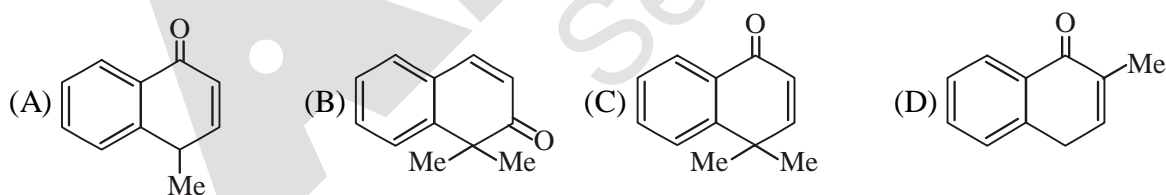
[IIT-JEE(ADV.)- 2009]

Q.17 The structure of the products **Q** and **R**, respectively, are

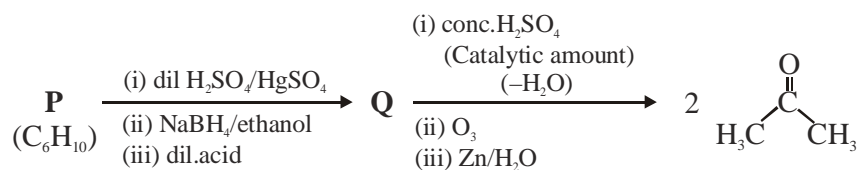
[IIT-JEE(ADV.)- 2009]

Q.18 The structure of the product **S** is

[IIT-JEE(ADV.)- 2009]

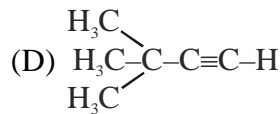
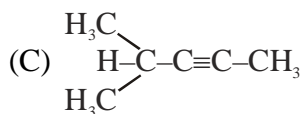
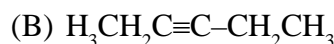
**Paragraph for Questions Nos. 19 to 20**

An acyclic hydrocarbon **P**, having molecular formula  $C_6H_{10}$ , gave acetone as the only organic product through the following sequence of reactions, in the which **Q** is an intermediate organic compound.



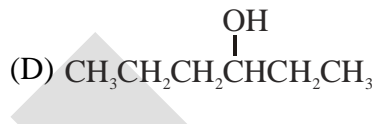
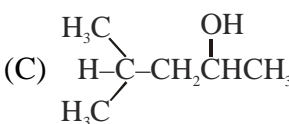
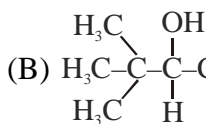
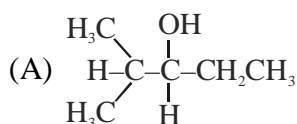
Q.19 The structure of compound P is -

[IIT-JEE(ADV.)- 2011]

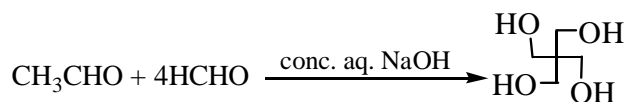


Q.20 The structure of the compound Q is -

[IIT-JEE(ADV.)- 2011]



Q.21 The number of aldol reaction(s) that occurs in the given transformation is [IIT-JEE(ADV.)- 2012]



(A) 1

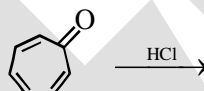
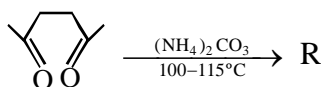
(B) 2

(C) 3

(D) 4

Q.22 Among P, Q, R and S, the aromatic compound(s) is / are :

[IIT-JEE(ADV.)- 2013]



(A) P

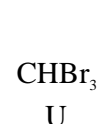
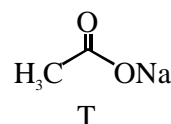
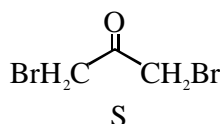
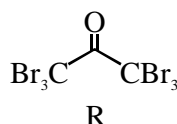
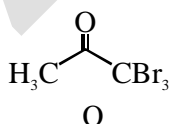
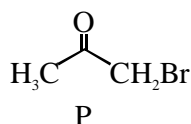
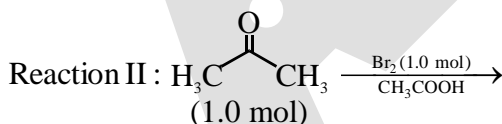
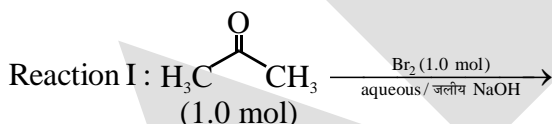
(B) Q

(C) R

(D) S

Q.23 After completion of the reactions (I and II), the organic compound(s) in the reaction mixtures is(are)

[IIT-JEE(ADV.)- 2013]



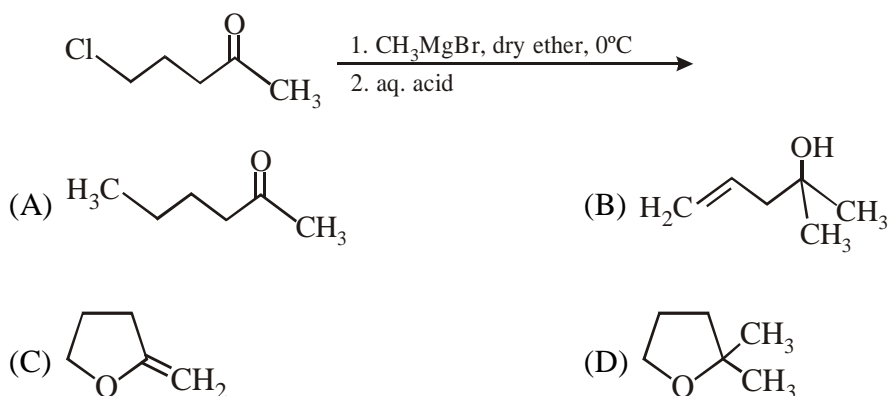
(A) Reaction I : P and Reaction II : P

(B) Reaction I : U, acetone and Reaction II : Q acetone

(C) Reaction I : T, U, acetone and Reaction II : P

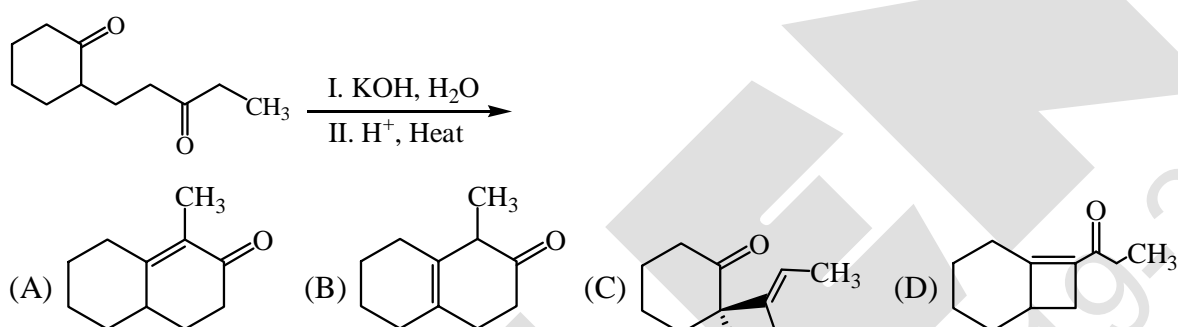
(D) Reaction I : R, acetone and Reaction II : S acetone

Q.24 The major product in the following reaction is [IIT-JEE(ADV.)- 2014]



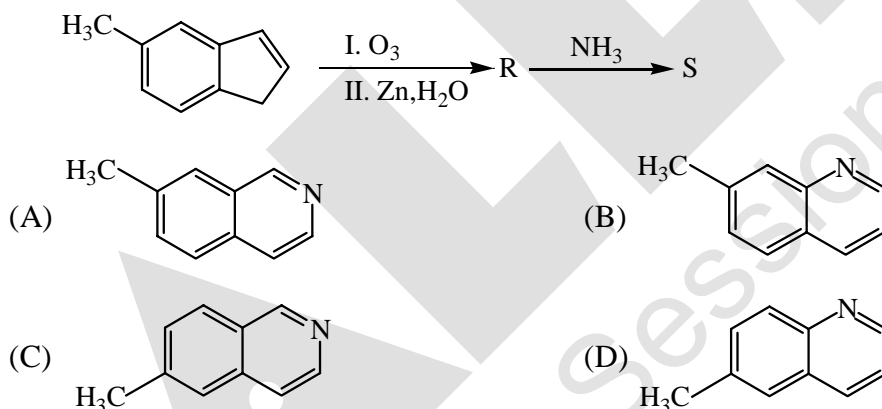
Q.25 The major product of the following reaction is -

[IIT-JEE(ADV.)- 2015]



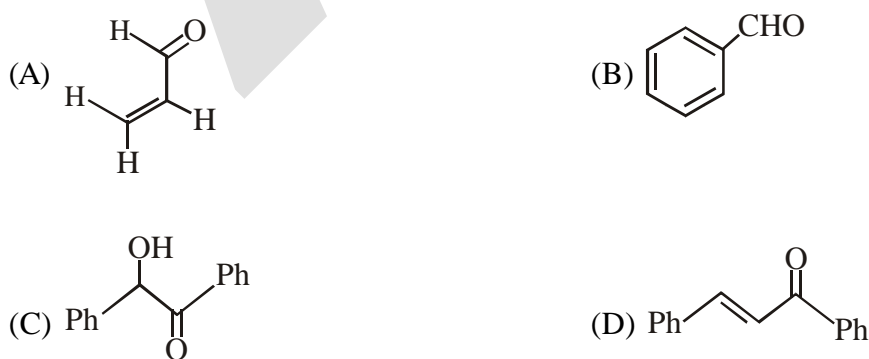
Q.26 In the following reactions, the product S is -

[IIT-JEE(ADV.)- 2015]



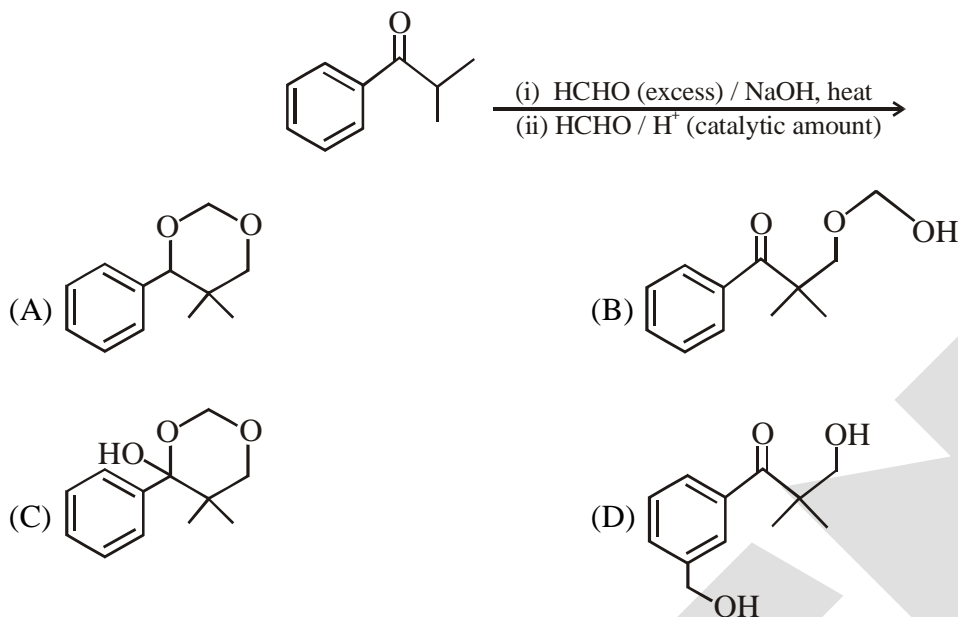
Q.27 Positive Tollen's test is observed for :

[IIT-JEE(ADV.)- 2016]



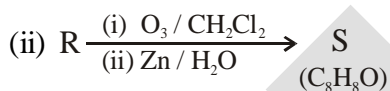
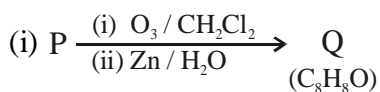
Q.28 The major product of the following reaction sequence is :

[IITJEE(ADV.)-2016]

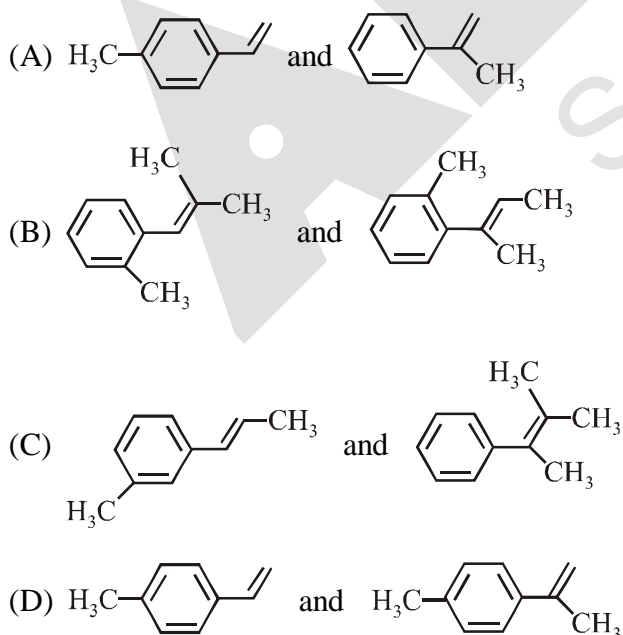


Q.29 Compound **P** and **R** upon ozonolysis produce **Q** and **S**, respectively. The molecular formula of **Q** and **S** is  $C_8H_8O$ . **Q** undergoes Cannizzaro reaction but not haloform reaction, whereas **S** undergoes haloform reaction but not Cannizzaro reaction :

[IIT-JEE(ADV.)- 2017]



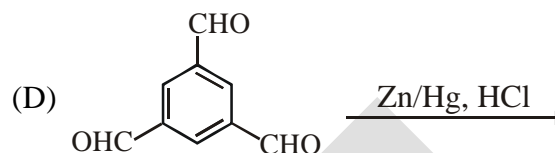
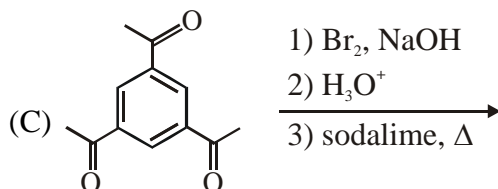
The option(s) with suitable combination of **P** and **R**, respectively, is(are)





30. The reaction(s) leading to the formation of 1,3,5-trimethylbenzene is (are)

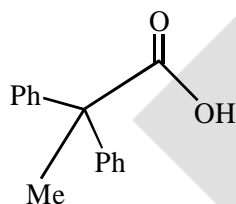
[IIT-JEE(ADV.)- 2018]



31. The desired product X can be prepared by reacting the major product of the reactions in LIST-I with one or more appropriate reagents in LIST-II.

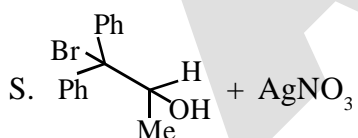
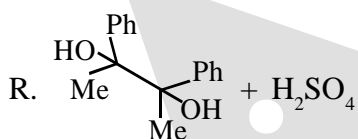
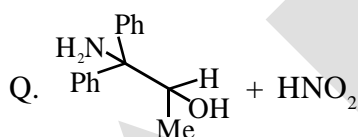
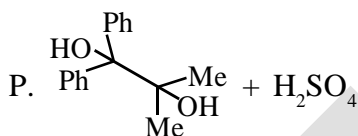
[IIT-JEE(Adv.)-2018]

(given, order of migratory aptitude: aryl > alkyl > hydrogen)



X

#### LIST-I



#### LIST-II

1.  $\text{I}_2, \text{NaOH}$

2.  $[\text{Ag}(\text{NH}_3)_2]\text{OH}$

3. Fehling solution

4.  $\text{HCHO}, \text{NaOH}$

5.  $\text{NaOBr}$

The correct option is

(A)  $\text{P} \rightarrow 1; \text{Q} \rightarrow 2,3; \text{R} \rightarrow 1,4; \text{S} \rightarrow 2,4$

(B)  $\text{P} \rightarrow 1,5; \text{Q} \rightarrow 3,4; \text{R} \rightarrow 4,5; \text{S} \rightarrow 3$

(C)  $\text{P} \rightarrow 1,5; \text{Q} \rightarrow 3,4; \text{R} \rightarrow 5; \text{S} \rightarrow 2,4$

(D)  $\text{P} \rightarrow 1,5; \text{Q} \rightarrow 2,3; \text{R} \rightarrow 1,5; \text{S} \rightarrow 2,3$

# ANSWER-KEY

## EXERCISE # I

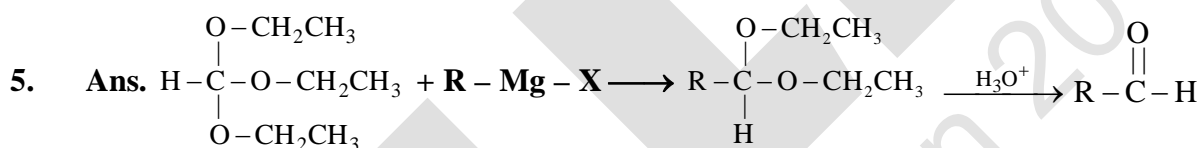
|    |          |    |          |    |          |    |          |
|----|----------|----|----------|----|----------|----|----------|
| 1  | Ans. (A) | 2  | Ans. (B) | 3  | Ans. (C) | 4  | Ans. (C) |
| 5  | Ans. (C) | 6  | Ans. (D) | 7  | Ans. (A) | 8  | Ans. (C) |
| 9  | Ans. (C) | 10 | Ans. (C) | 11 | Ans. (A) | 12 | Ans. (D) |
| 13 | Ans. (C) | 14 | Ans. (C) | 15 | Ans. (B) | 16 | Ans. (D) |
| 17 | Ans. (C) | 18 | Ans. (A) | 19 | Ans. (D) | 20 | Ans. (D) |
| 21 | Ans. (C) | 22 | Ans. (D) | 23 | Ans. (C) | 24 | Ans. (B) |
| 25 | Ans. (A) | 26 | Ans. (D) | 27 | Ans. (C) | 28 | Ans. (D) |
| 29 | Ans. (C) | 30 | Ans. (D) |    |          |    |          |

## EXERCISE # II

|    |            |    |                |    |                                      |    |            |
|----|------------|----|----------------|----|--------------------------------------|----|------------|
| 1  | Ans. (A,B) | 2  | Ans. (C,D)     | 3  | Ans. (A,B,C)                         | 4  | Ans. (B,C) |
| 5  | Ans. (A,B) | 6  | Ans. (A,B,C,D) | 7  | Ans. (A,B,C)                         | 8  | Ans. (B,C) |
| 9  | Ans. (A,D) | 10 | Ans. (D)       | 11 | Ans. (D)                             | 12 | Ans. (B)   |
| 13 | Ans. (B)   | 14 | Ans. (A,B,C)   | 15 | Ans. (A)→R ; (B)→Q,S ; (C)→S ; (D)→P |    |            |

## EXERCISE # III

- Ans. (A) P,Q,S ; (B) P,Q,S ; (C) P,Q,S ; (D) P,Q,S
- Ans.  $3 > 2 > 1 > 4$
- Ans. (C)
- Ans. (A)

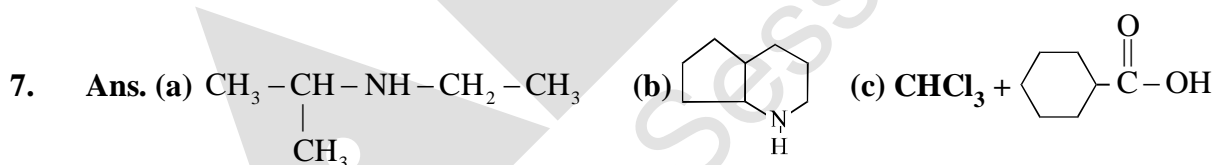


Ethyl orthoformate

Acetal

aldehyde

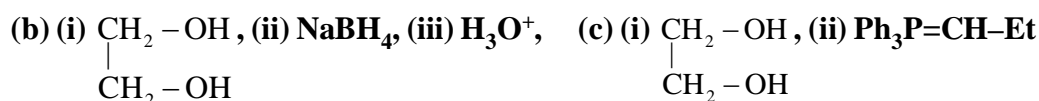
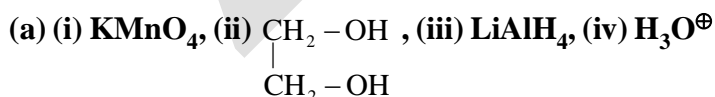
- Ans.  $\text{H}^+/\text{Br}_2$  ;  $\text{H}_2/\text{Ni}$  ;  $\text{NaOH}$



- Ans. (B,C)

- Ans. (B)

- Ans.



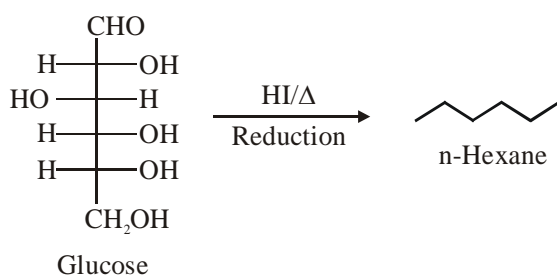
- Ans. (B)

- Ans. (D)

## EXERCISE # IV (MAINS)

- |                 |              |              |              |
|-----------------|--------------|--------------|--------------|
| 1. Ans. (4)     | 2. Ans. (2)  | 3. Ans. (1)  | 4. Ans. (2)  |
| 5. Ans. (4)     | 6. Ans. (2)  | 7. Ans. (4)  | 8. Ans. (3)  |
| 9. Ans. (4)     | 10. Ans. (4) | 11. Ans. (2) | 12. Ans. (4) |
| 13. Ans. (4)    | 14. Ans. (4) | 15. Ans. (4) | 16. Ans. (3) |
| 17. Ans. (1, 3) | 18. Ans. (2) | 19. Ans. (1) | 20. Ans. (2) |
| 21. Ans. (1)    | 22. Ans. (2) | 23. Ans. (2) | 24. Ans. (1) |
| 25. Ans. (4)    | 26. Ans. (1) | 27. Ans. (3) |              |
| 28. Ans. (4)    |              |              |              |

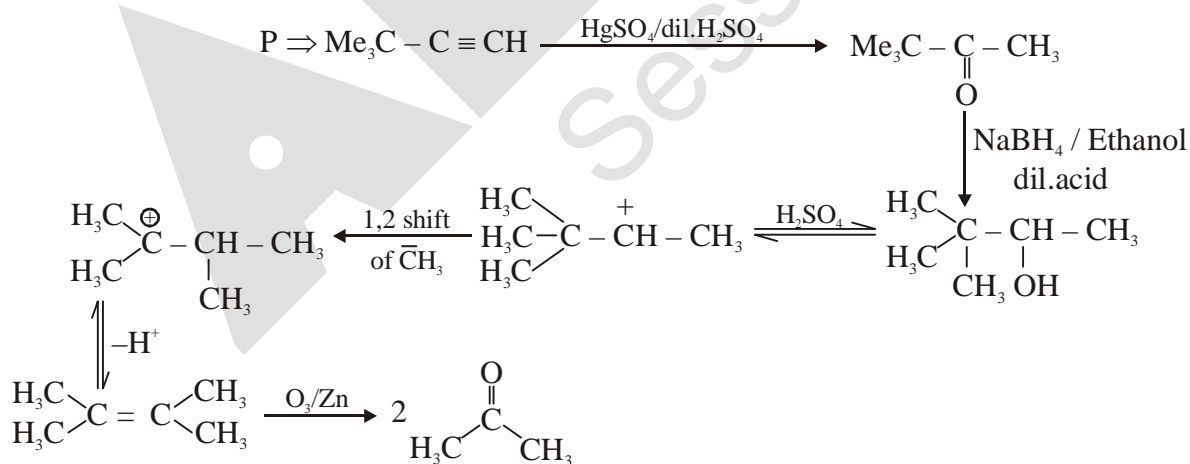
Sol.



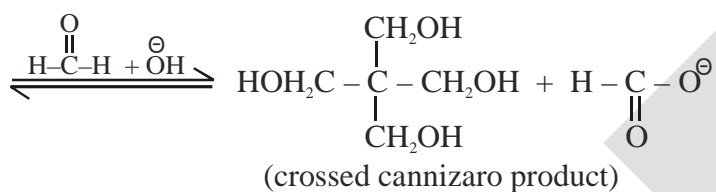
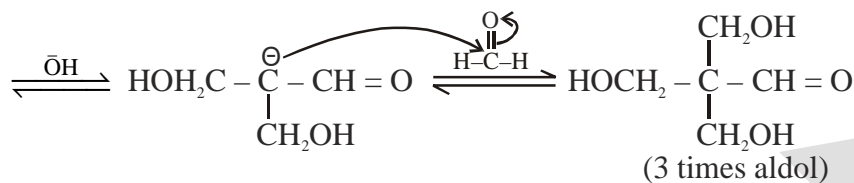
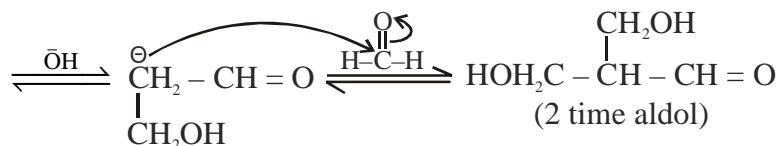
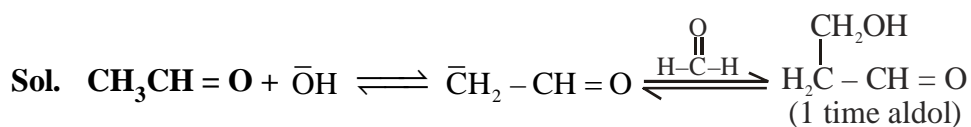
- |              |              |              |              |
|--------------|--------------|--------------|--------------|
| 29. Ans. (1) | 30. Ans. (2) | 31. Ans. (1) | 32. Ans. (2) |
|--------------|--------------|--------------|--------------|

## EXERCISE-IV # (A) (OBJECTIVE QUESTIONS)

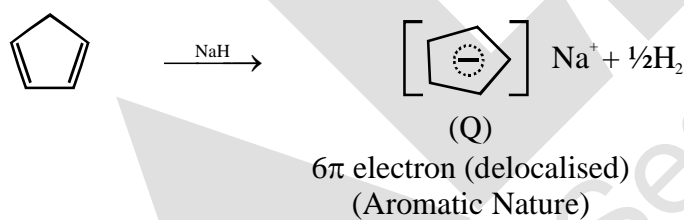
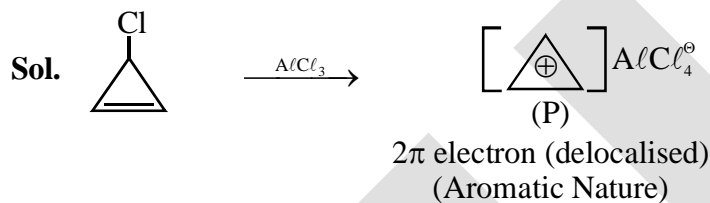
- |                                             |              |              |              |
|---------------------------------------------|--------------|--------------|--------------|
| 1. Ans. (B)                                 | 2. Ans. (A)  | 3. Ans. (C)  | 4. Ans. (A)  |
| 5. Ans. (C)                                 | 6. Ans. (D)  | 7. Ans. (C)  | 8. Ans. (C)  |
| 9. Ans. (B)                                 | 10. Ans. (A) | 11. Ans. (C) |              |
| 12. Ans. (A) P,S; (B) Q; (C) Q,R,S; (D) Q,R | 13. Ans. (B) | 14. Ans. (A) |              |
| 15. Ans. (D)                                | 16. Ans. (B) | 17. Ans. (A) | 18. Ans. (B) |
| 19. Ans. (D)                                |              |              |              |
| 20. Ans. (B)                                |              |              |              |



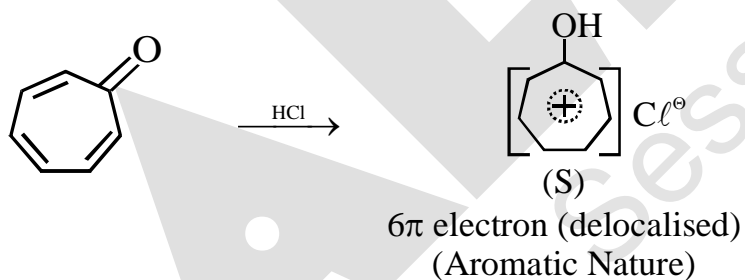
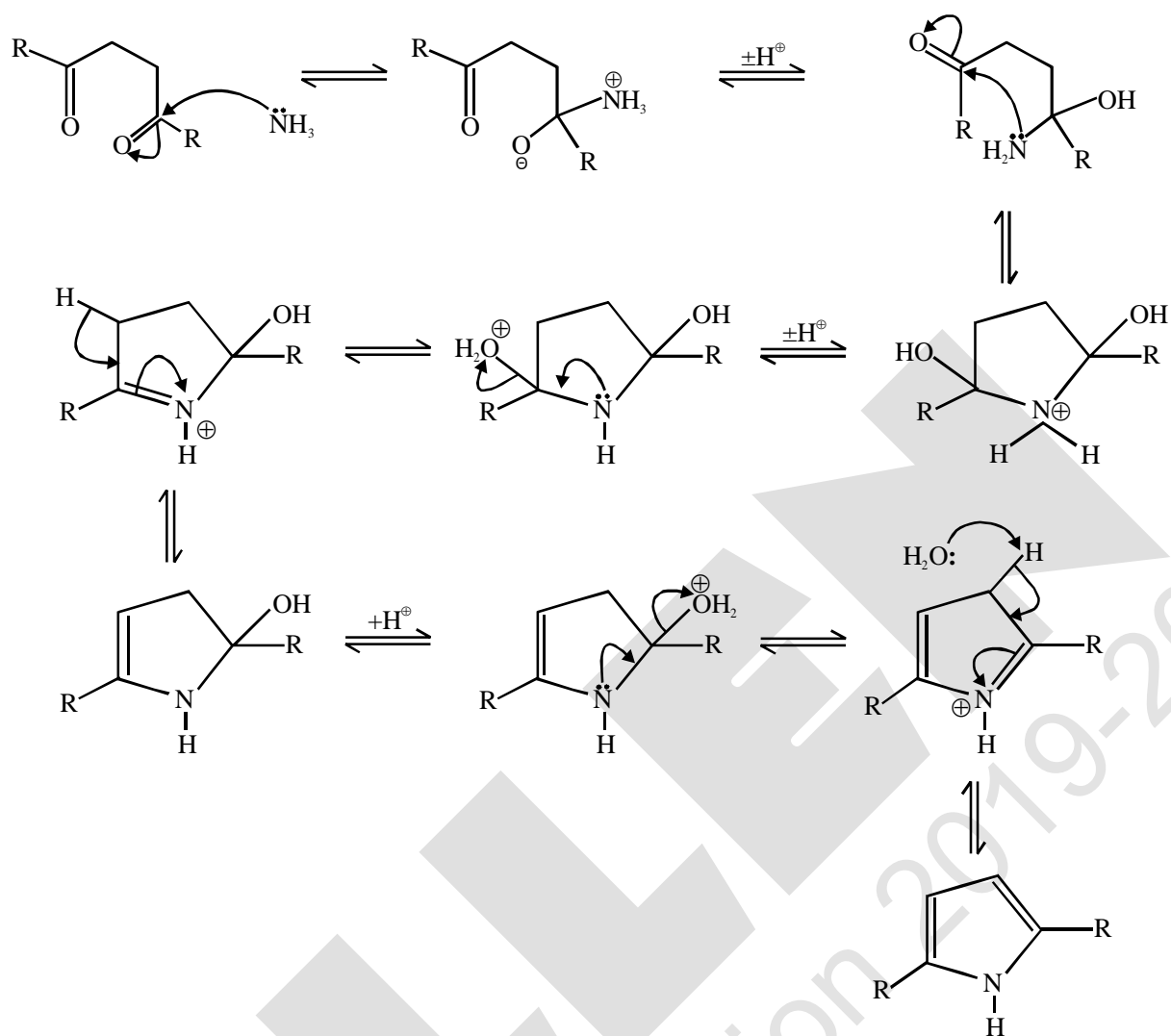
21. Ans. (C)



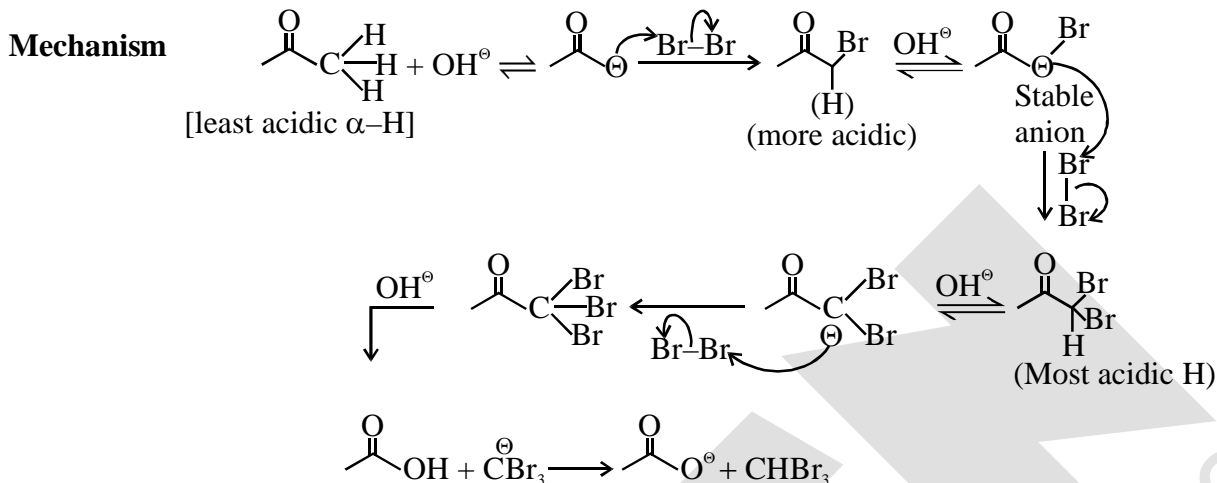
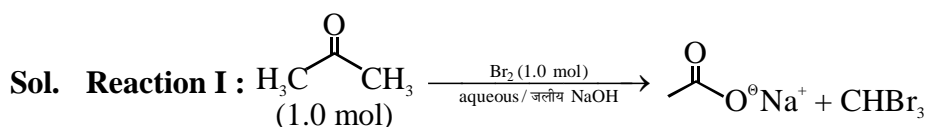
22. Ans. (A,B,C,D)



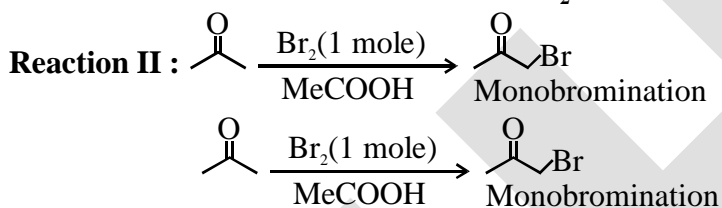
Mechanism :



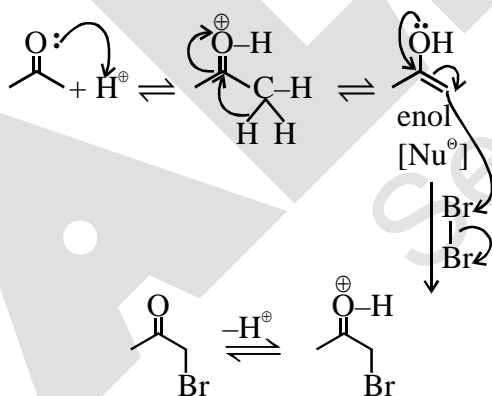
23. Ans. (C)



In basic medium halogenation does not stop with replacement of just one hydrogen and poly halogenation takes place because  $\alpha$ -haloketones are more reactive towards base and haloform reaction takes place. In above reaction  $\text{Br}_2$  is limiting agents.

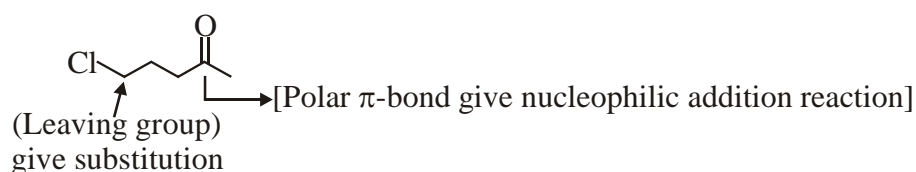


**Mechanism :**

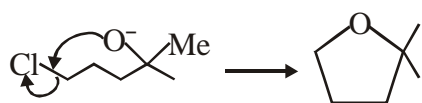


Further bromination is less favourable because of less amount of  $\text{Br}_2$

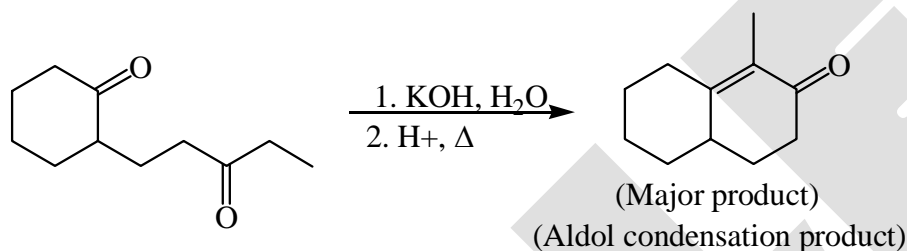
24. Ans. (D)

(i) Grignard prefer to give nucleophilic addition on polar  $\pi$ -bond and form anion intermediate.

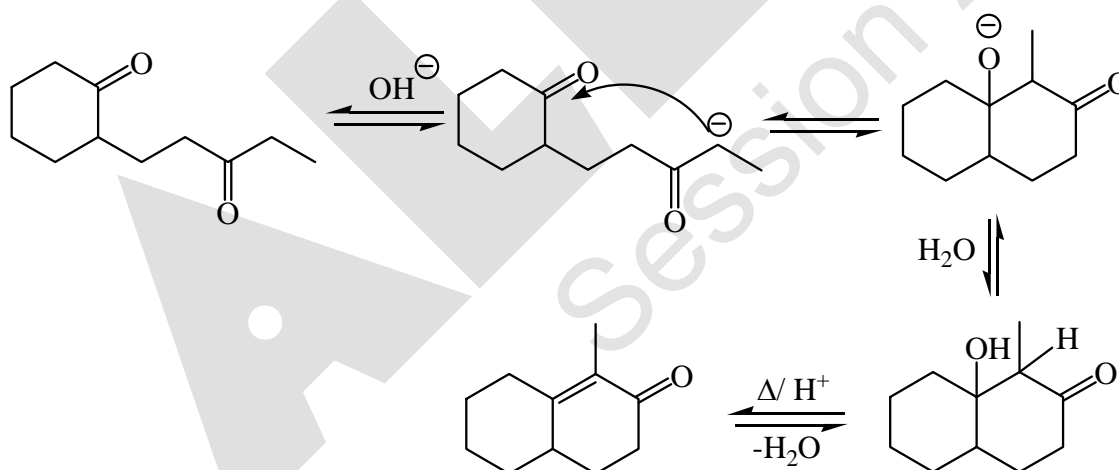
(ii) In next step anion give intramolecular nucleophilic substitution reaction &amp; form 5 membered ring.



25. Ans. (A)

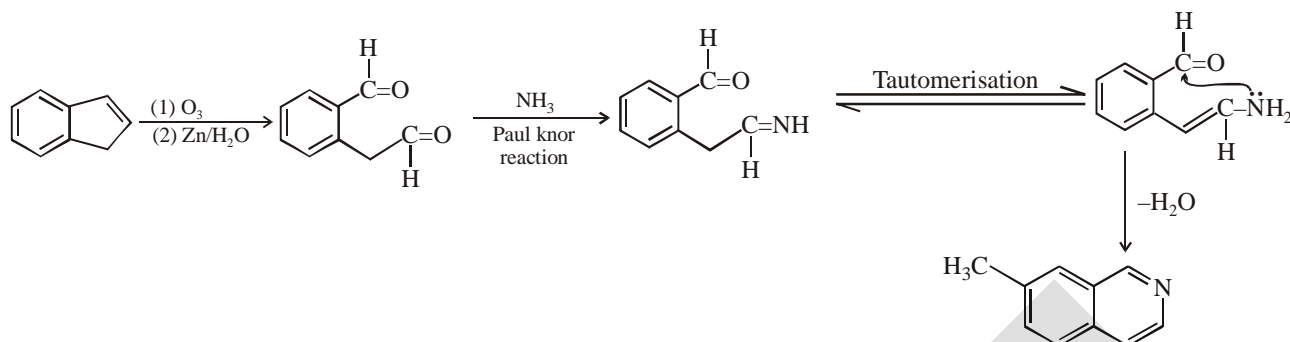


Mechanism :



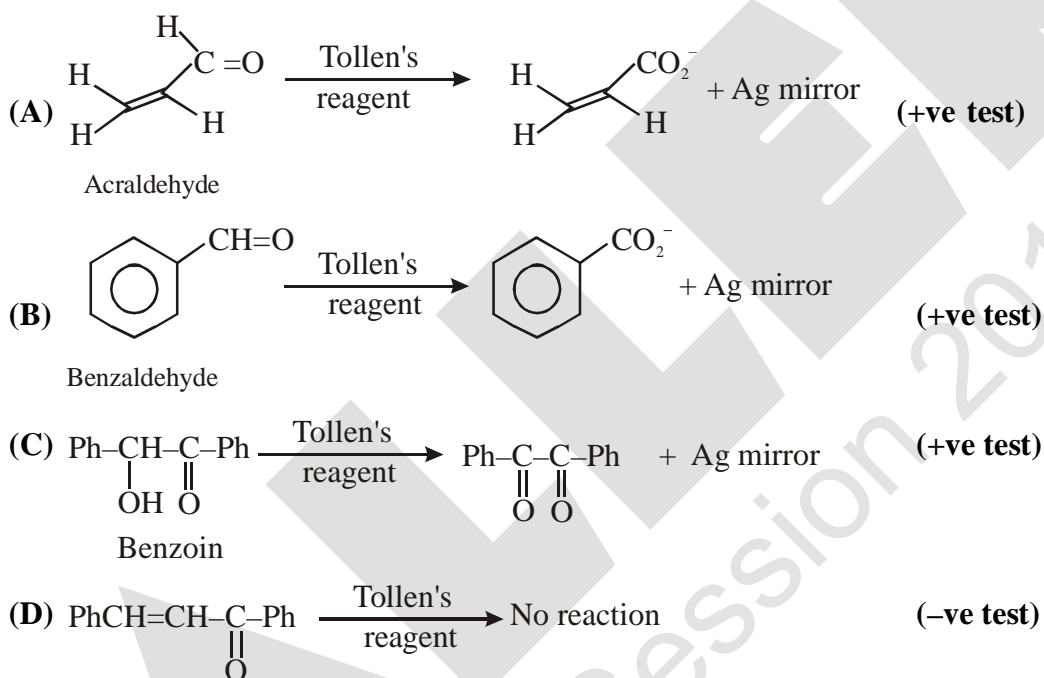
26. Ans.(A)

Sol.



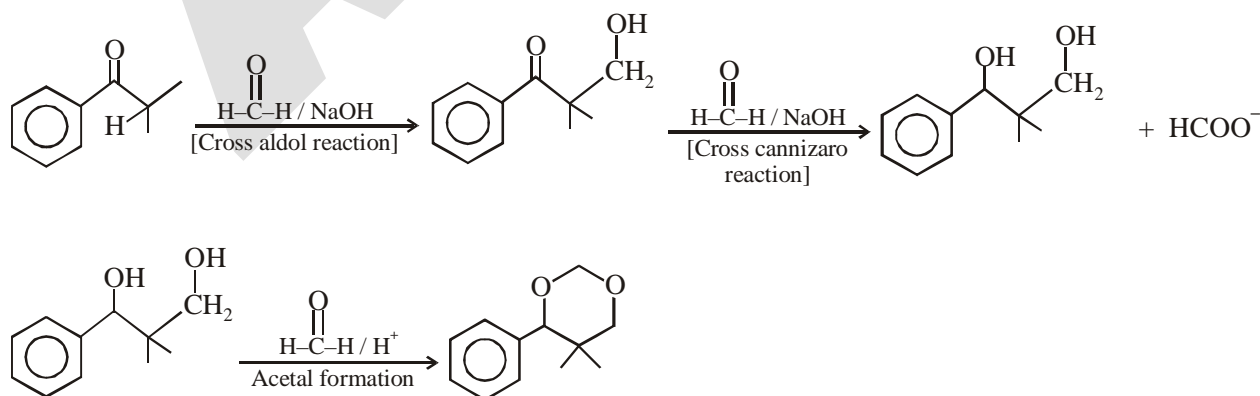
27. Ans. (A,B,C)

Sol. Tollens's test is given by compounds having aldehyde group. Also  $\alpha$ -hydroxy carbonyl gives positive tollens's test.



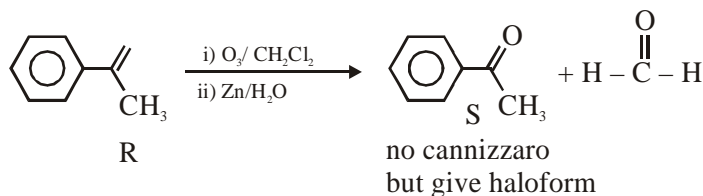
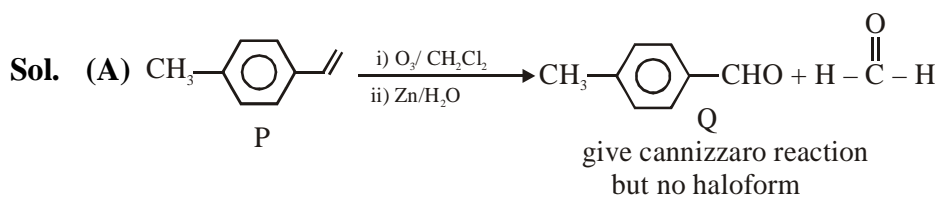
28. Ans. (A)

Sol.

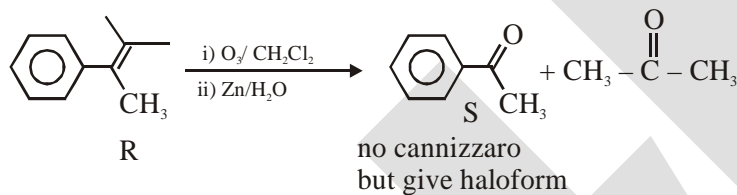
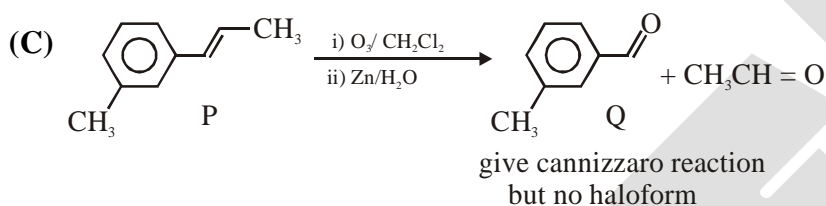




29. Ans. (A,C)

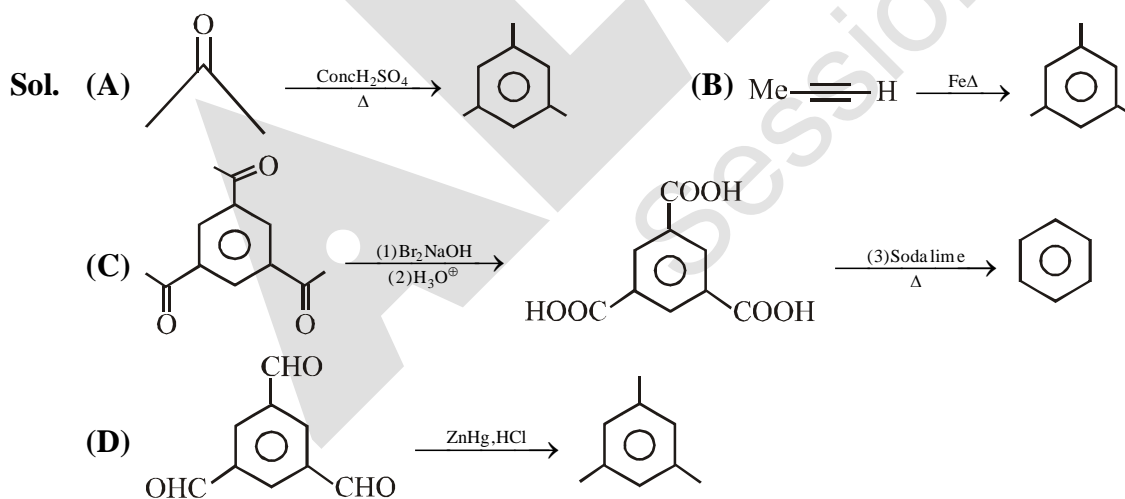


(B) Product of ozonolysis of R is having 9 carbon.



(D) Product of ozonolysis of R is having 9 carbon.

30. Ans. (A,B,D)

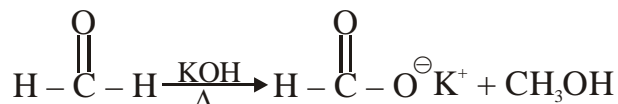


31. Ans. (D)

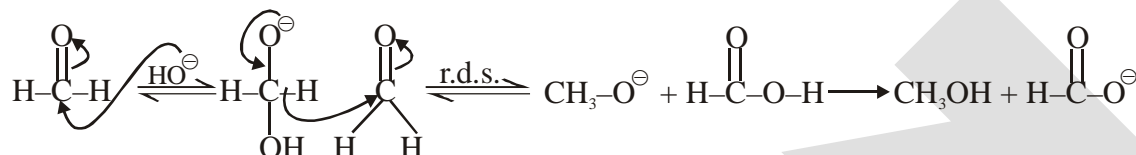
# ALDOL & SIMILAR NAME REACTIONS

## (1) CANNIZARO REACTION

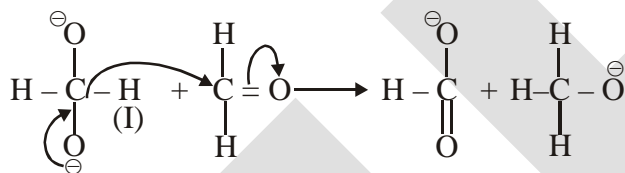
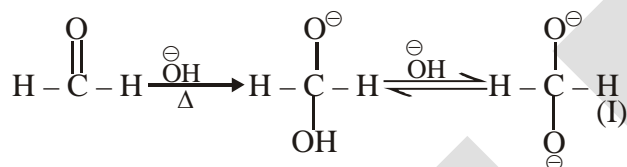
This reaction is given by aldehyde having no  $\alpha$ -hydrogen in the presence of conc.  $\text{NaOH}/\Delta$  or  $\text{KOH}/\Delta$ .



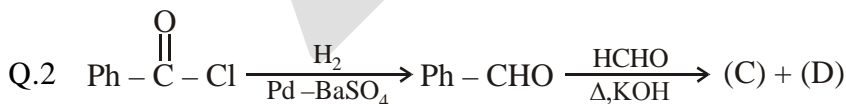
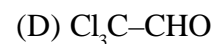
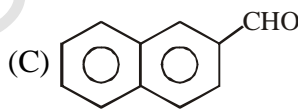
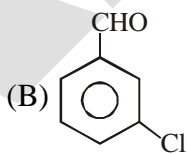
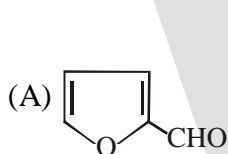
**Mechanism :**



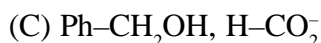
In the presence of a very strong concentration of alkali, aldehyde first forms a doubly charged anion (I) from which a hydride anion is transferred to the second molecule of the aldehyde to form acid and an alkoxide ion. Subsequently, the alkoxide ion acquires a proton from the solvent.

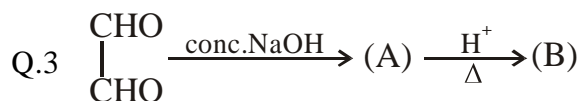


Q.1 Which of following will not undergo Cannizzaro reaction

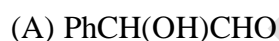
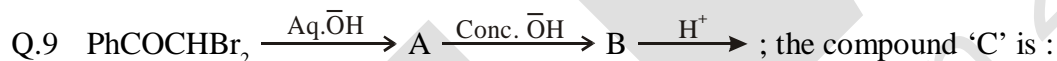
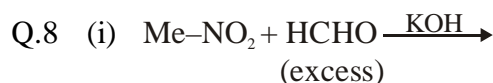
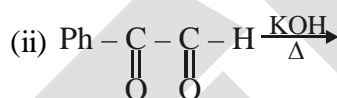
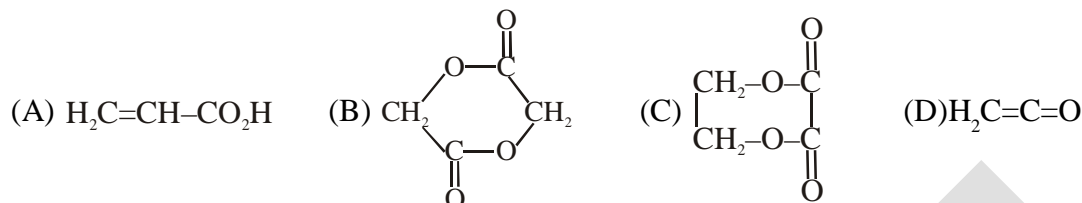


Product (C) & (D) are :





Product (B) is :

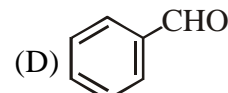
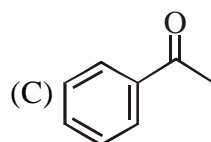
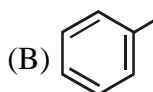
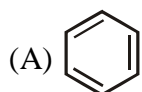
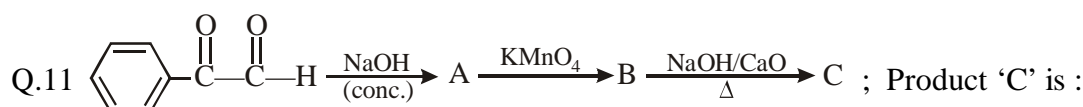
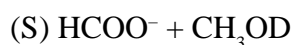
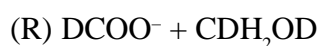
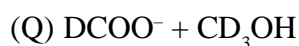
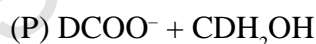


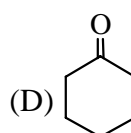
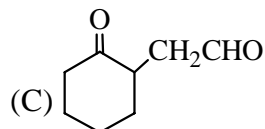
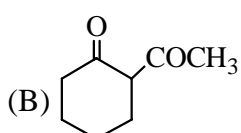
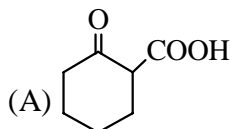
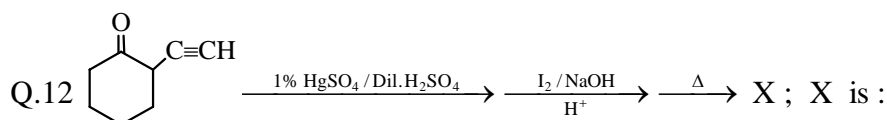
Q.10 Match the column :

**Column - I**

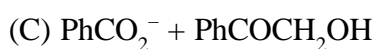
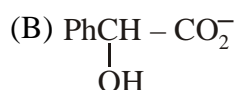


**Column - II**

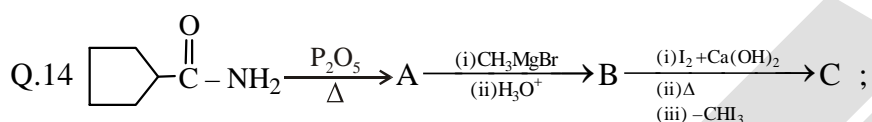




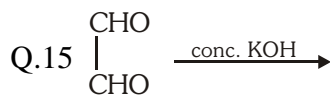
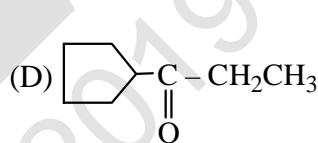
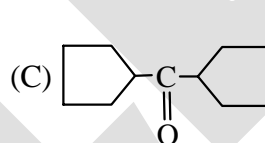
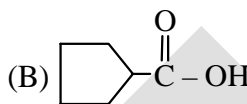
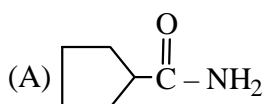
Q.13 The cannizzaro reaction of  $\text{PhCOCHO}$  forms the product(s)



(D) Both (A) and (C)



Product is:

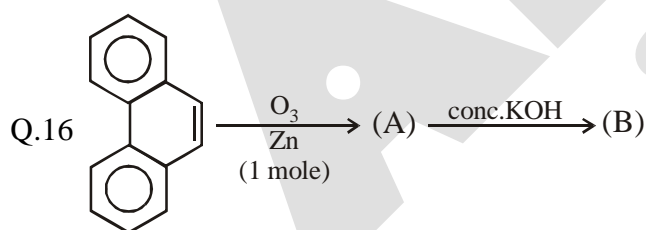


True about this reaction is / are

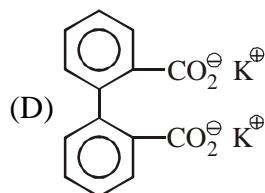
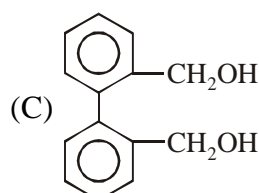
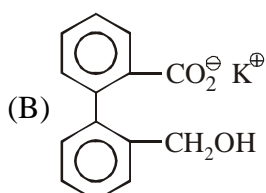
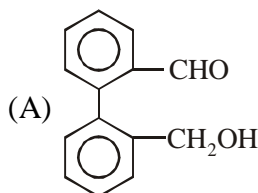
(A) Cannizzaro name is associated with this reaction (B) It is a disproportionation reaction

(C) It is a bimolecular reaction in r.d.s.

(D) All of these



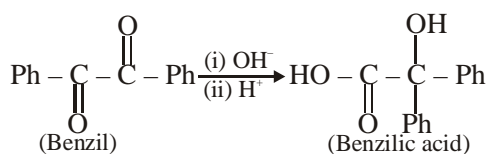
End product (B) of above reaction is :



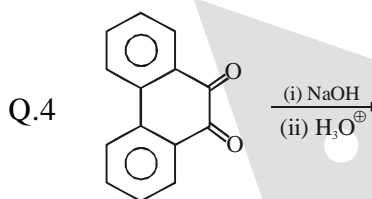
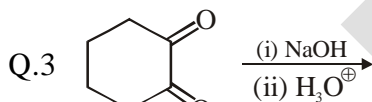
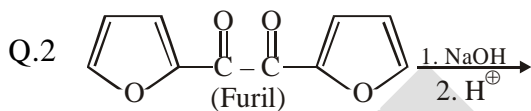
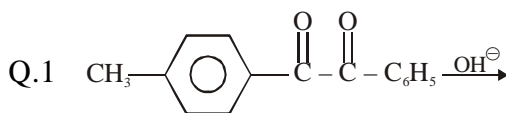
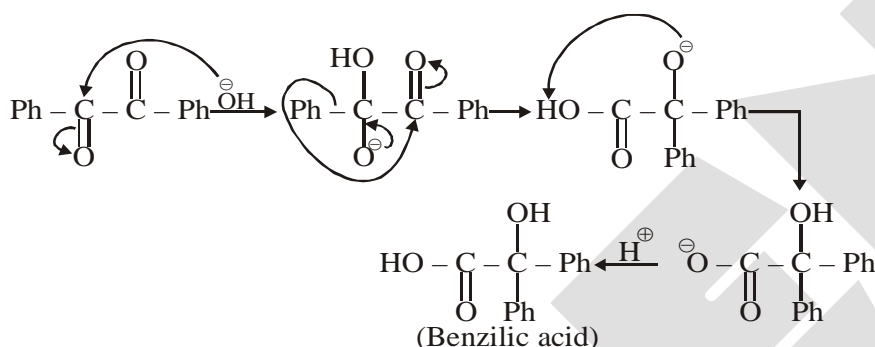


## (2) BENZIL-BENZILIC REARRANGEMENT OR BENZILIC ACID REARRANGEMENT

The base catalysed reaction of 1,2-diketones to a salt of  $\alpha$ -hydroxy carboxylic acid is known as Benzilic acid rearrangement, this reaction is mainly applicable when aryl group is present on both carbonyl carbons.

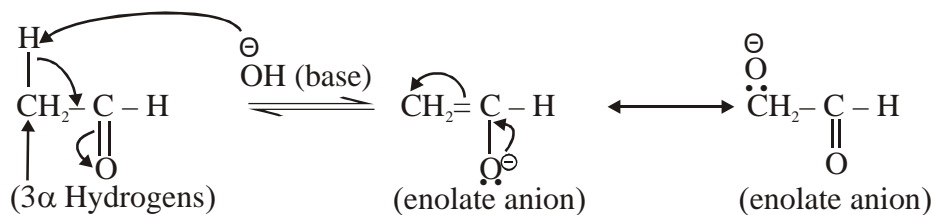


**Mechanism :**



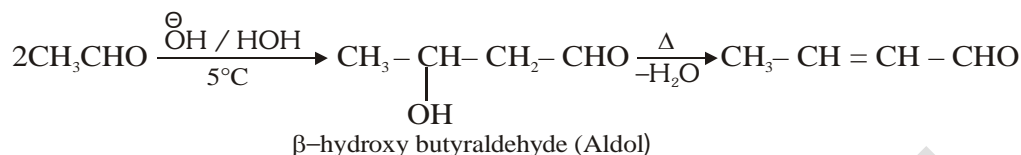
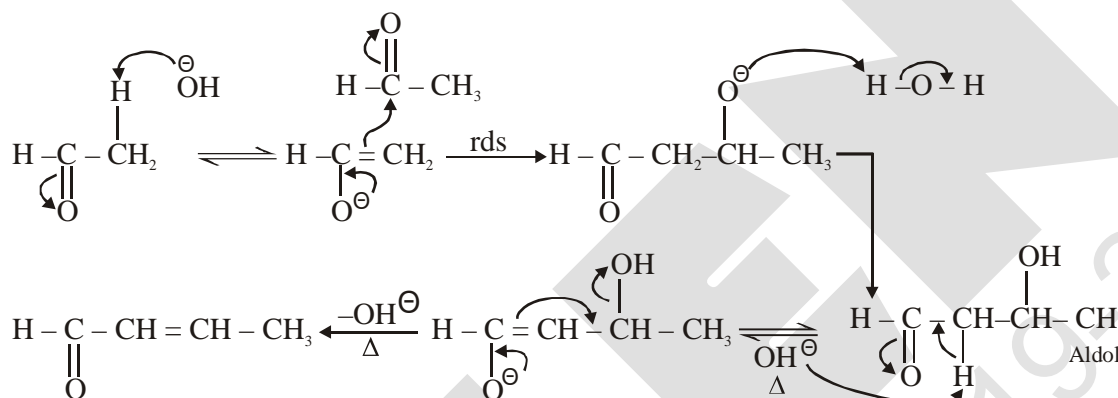
## (3) ALDOL CONDENSATION

The  $\alpha$ -hydrogen of carbonyl compounds are acidic due to the fact that the anion (enolate ion) is stabilized by resonance.



**Base catalysed Aldol**

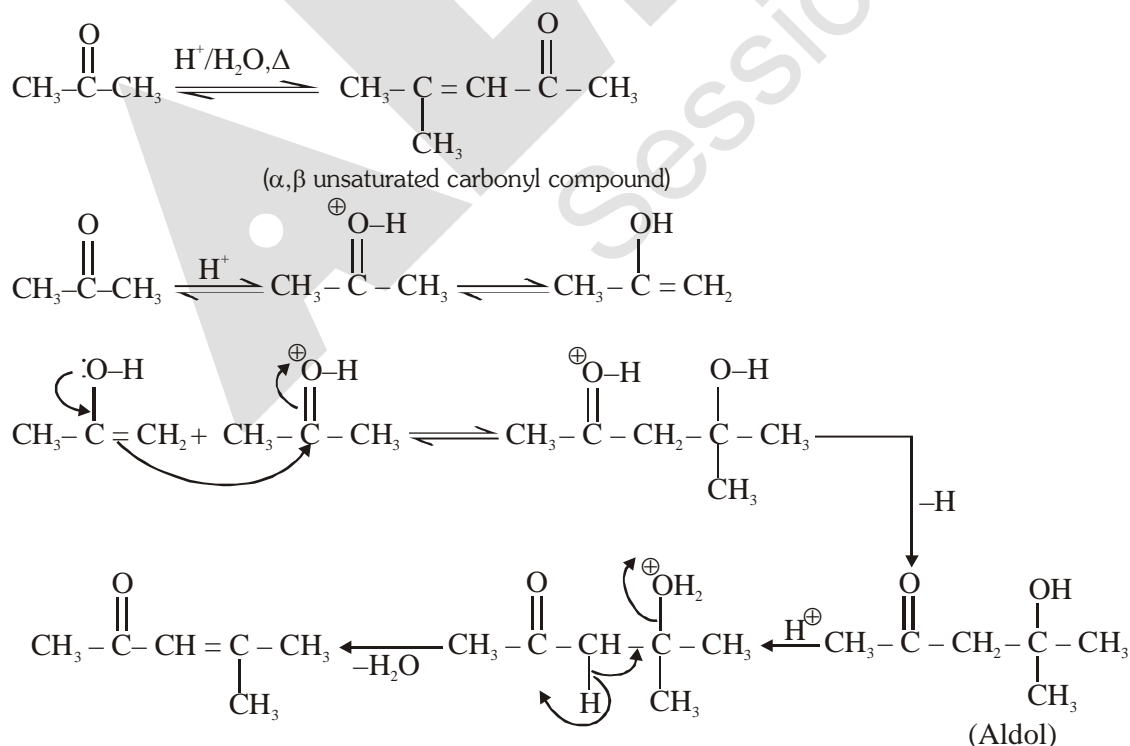
In aqueous base, two acetaldehyde molecules react to form  $\beta$ -hydroxy aldehyde called aldol. The reaction is called Aldol condensation. The enolate ion is the intermediate in the aldol condensation of aldehyde and ketone. Acetaldehyde for instance, forms a dimeric product aldol in presence of a dilute base ( $\approx 10\%$  NaOH)

**Mechanism :**

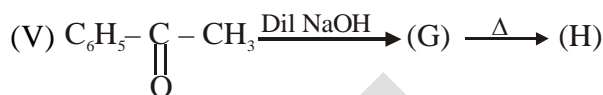
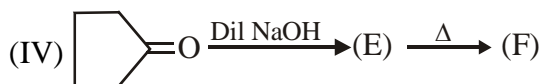
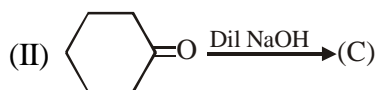
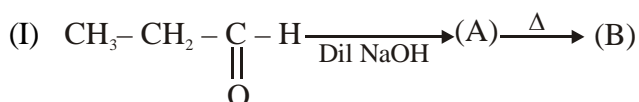
Aldols are stable and may be isolated. They, however can be dehydrated easily by heating the basic reaction mixture or by a separate acid catalyzed reaction. Thus if the above reaction is heated the product is dehydrated to 2-butenal (crotonaldehyde).

**Acid catalysed Aldol**

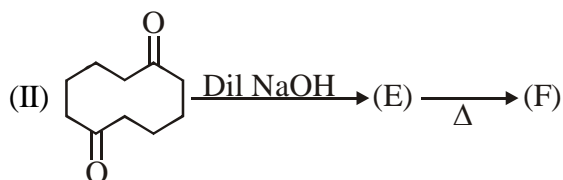
In acid catalysed aldol condensation enol form of carbonyl is the nucleophile in place of enolate.

**Mechanism :**

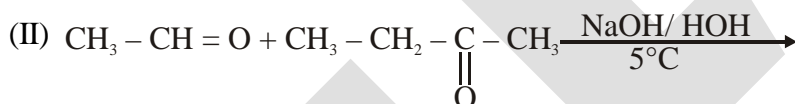
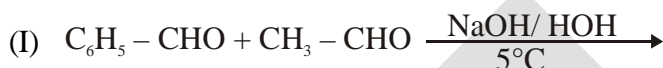
Q.1 Write the product and mechanism for given reactions.



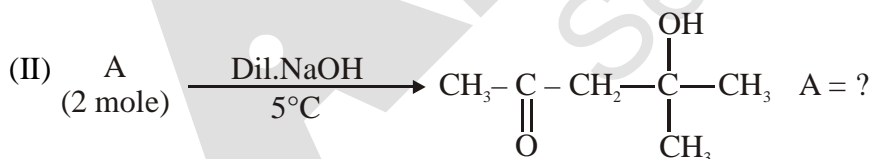
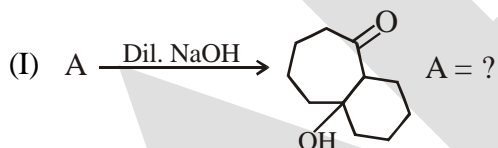
Q.2 Identify the intramolecular aldol product ?



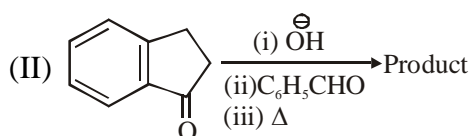
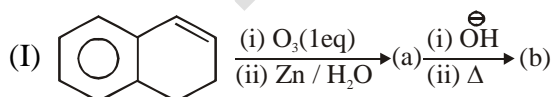
Q.3 Find out the total number of possible aldol products (including and excluding stereo products).



Q.4 Identify the structure of substrate ?

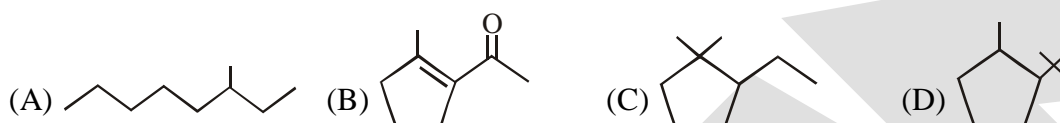
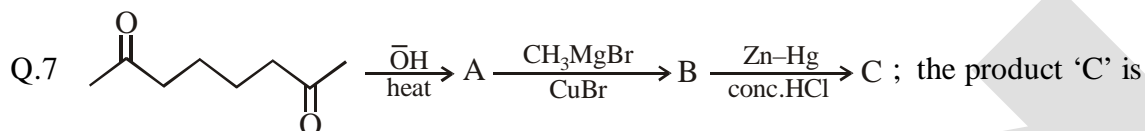
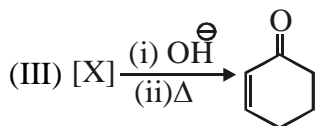
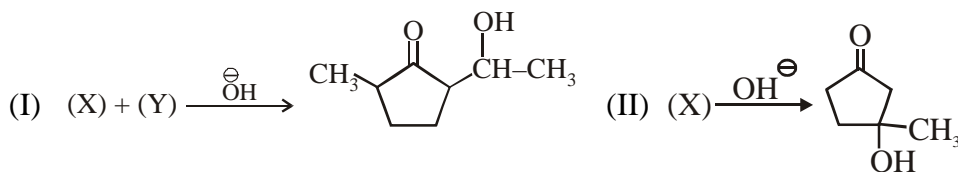


Q.5 Complete reaction sequence :

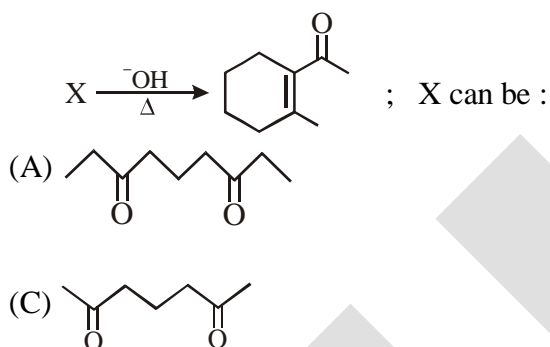




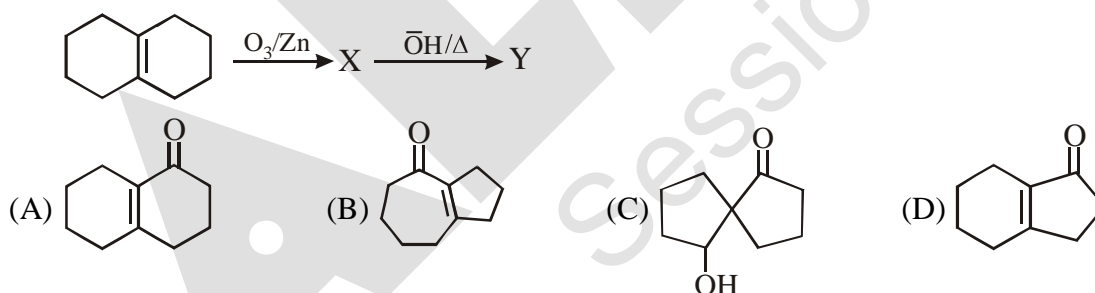
Q.6 Complete the following reactions :



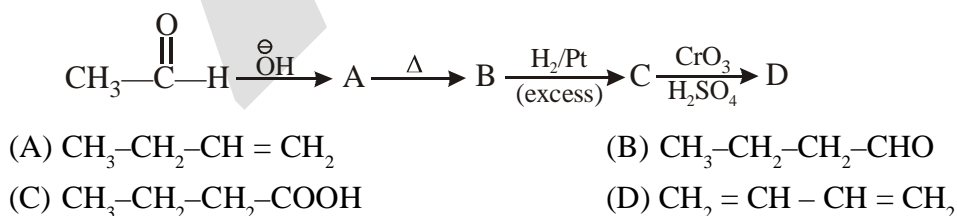
Q.8 Consider following intramolecular aldol condensation reaction :



Q.9 Product 'Y' formed in the given reaction is :



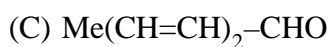
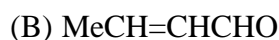
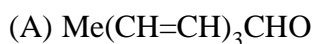
Q.10 Product 'D' is :



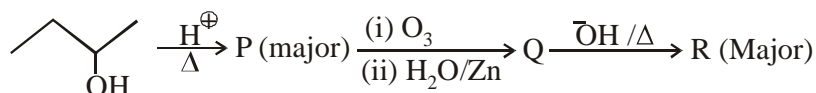
Q.11  $\text{CH}_3\text{CH}=\text{CHCHO} \xrightarrow[\text{aldol}]{\text{OH}^\ominus} \xrightarrow{\Delta} \text{A}$ , A is :



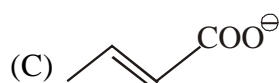
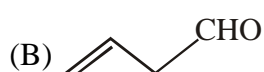
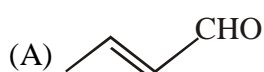
Q.12  $\text{MeCHO} \xrightarrow{\text{NaOH}, \Delta} \text{A} \xrightarrow{\text{NaOH}, \Delta} \text{B}$  ; B is :



Q.13 For the given reaction :

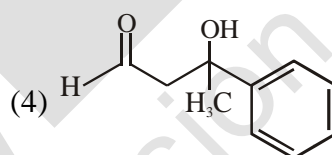
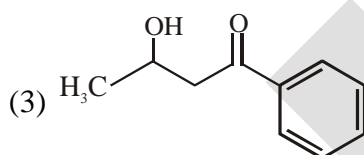
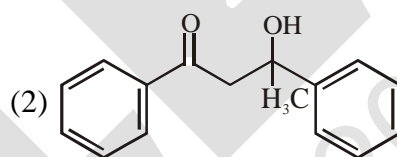
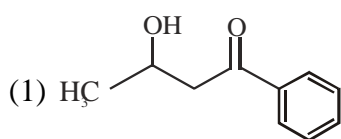
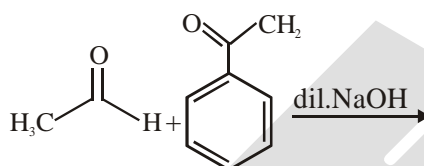


The (R) is :



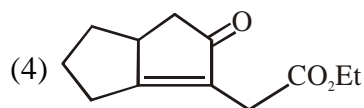
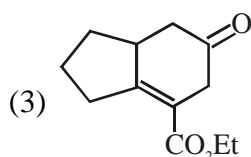
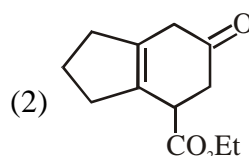
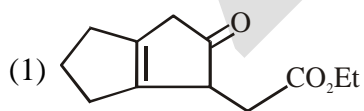
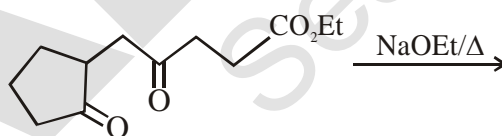
Q.14 The major product formed in the following reaction is:

[JEE-MAIN (JANUARY)-2019]



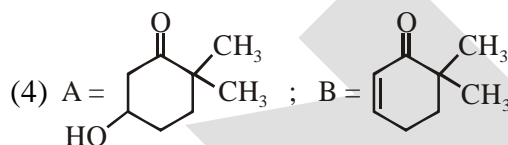
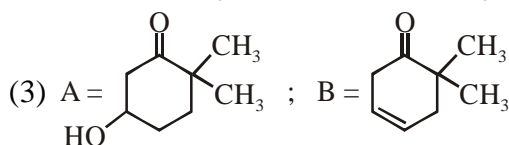
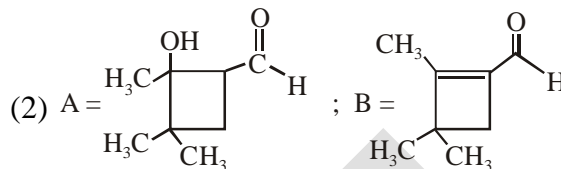
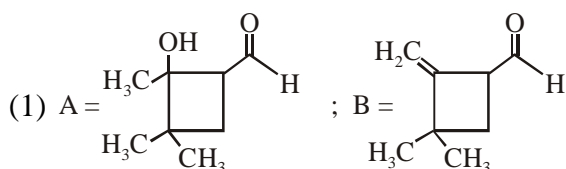
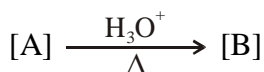
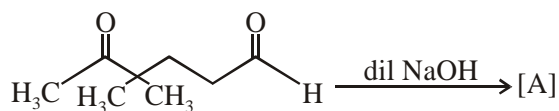
Q.15 The major product obtained in the following reaction is :

[JEE-MAIN (JANUARY)-2019]



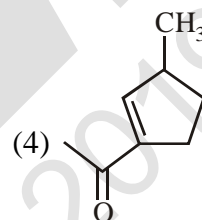
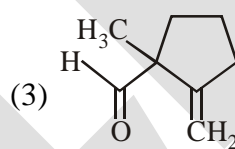
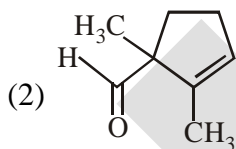
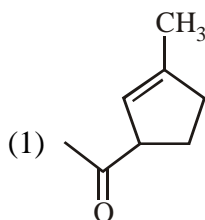
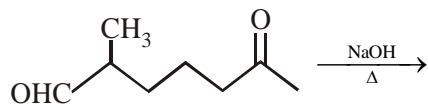
Q.16 In the following reactions, products A and B are :

[JEE-MAIN (JANUARY)-2019]



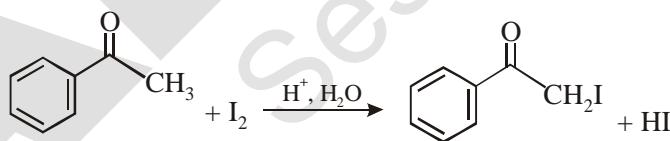
Q.17 The major product obtained in the following reaction is

[JEE-MAIN (APRIL)-2019]

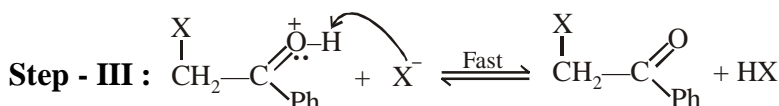
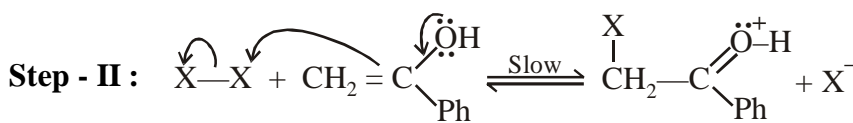
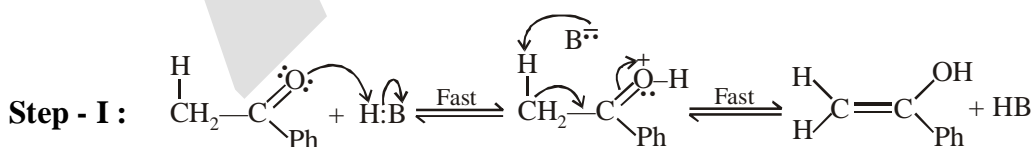


#### (4) HALOGENATION OF THE $\alpha$ -CARBON OF ALDEHYDES AND KETONES

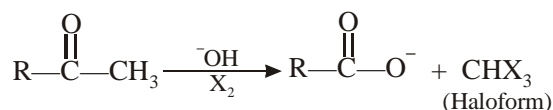
**I<sup>st</sup> Acid-Catalyzed halogenation :** - When  $\text{Br}_2$ ,  $\text{Cl}_2$  and  $\text{I}_2$  is added to an acidic solution of an aldehyde or a ketone, a halogen replaces one of the  $\alpha$ -hydrogens of the carbonyl compound. Halogenation takes place through the slow formation of an enol followed by rapid reaction of the enol with the halogen.



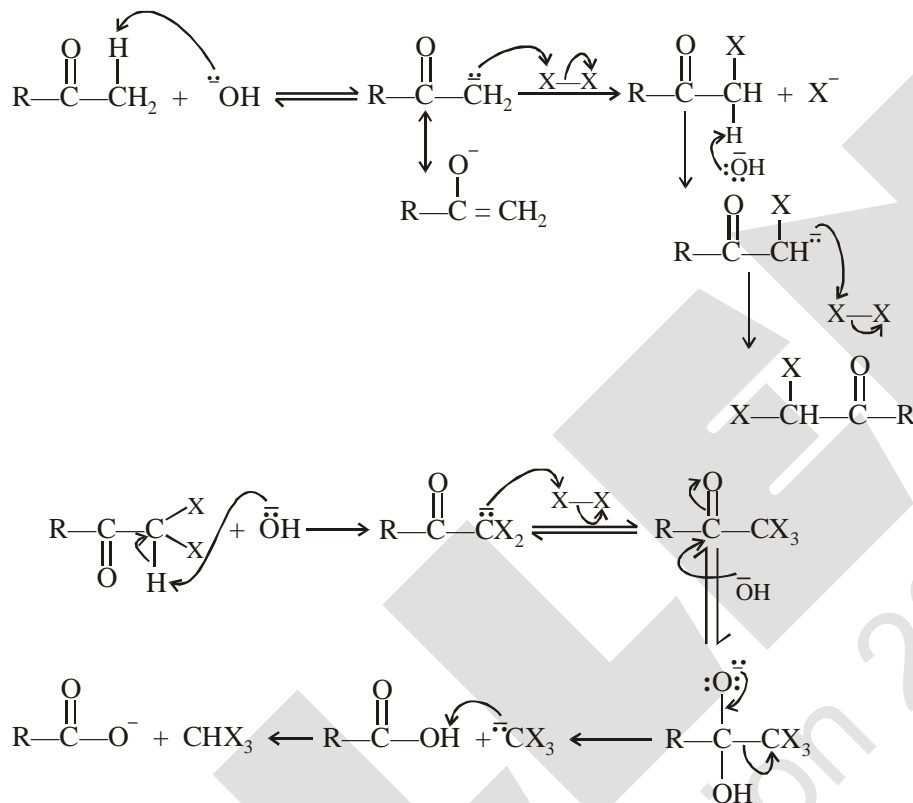
#### Mechanism :



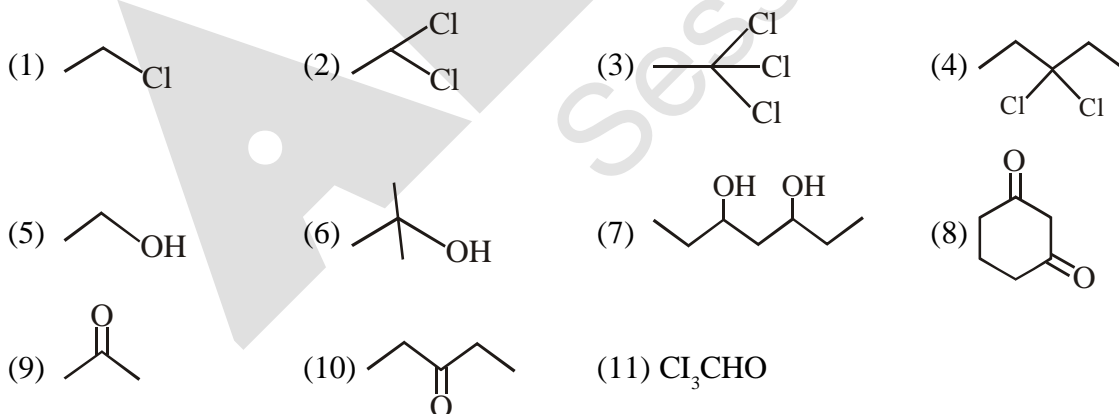
**II<sup>nd</sup> Base-Catalyzed halogenation :** - In the presence of excess base and excess halogen, a methyl ketone is converted first into a trihalo-substituted ketone and then into a carboxylic acid.



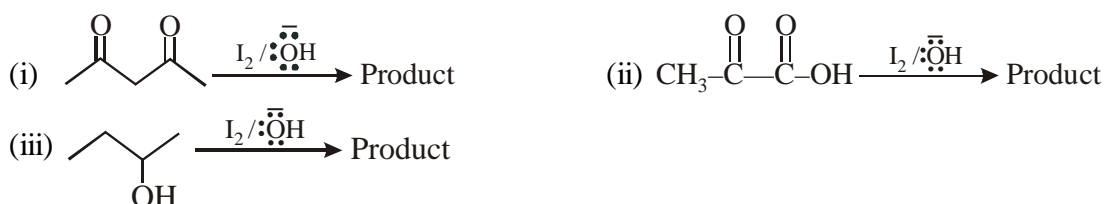
**Mechanism :**



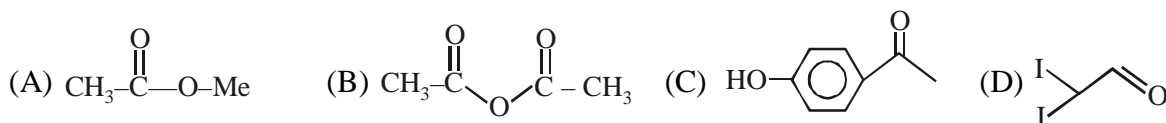
Q.1 Identify the compounds which can show iodoform test and complete the reaction ?



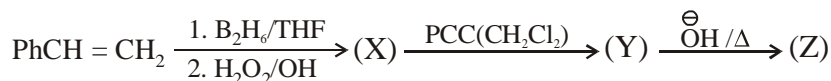
Q.2 Complete the following given reaction :



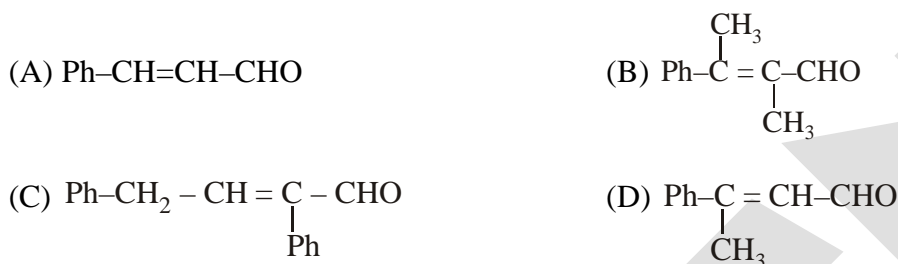
Q.3 Select the compound which does not show haloform reaction is/are :



Q.4 For the reaction



(Z) is :



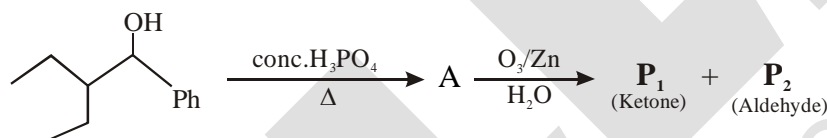
Q.5 Two isomeric ketones, 3-pentanone and 2-pentanone can be distinguished by :



Q.6 Which of the reagent is used to convert 2-Butanone into propanoic acid -



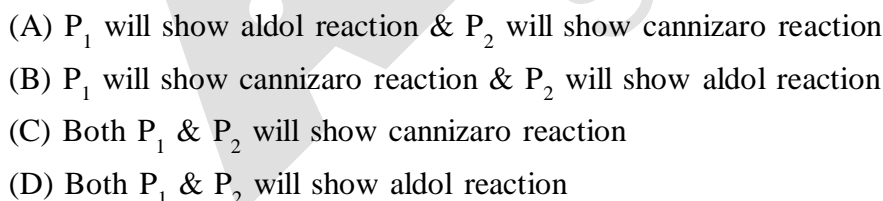
**Paragraph for Q.07 to Q.09**



Q.7 Which one of the following reagent is best suitable for distinction between  $\text{P}_1$  and  $\text{P}_2$  -

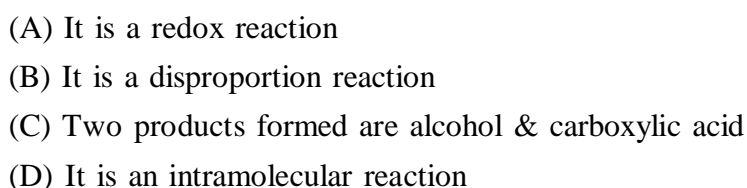


Q.8 Select the correct statement among the following -

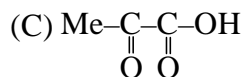
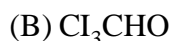
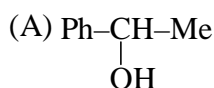


Q.9  $\text{P}_2 \xrightarrow[\text{(ii) H}^+]{\text{conc. NaOH}}$  products

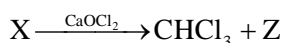
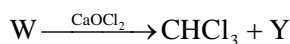
Select incorrect statement for the above reaction -



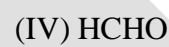
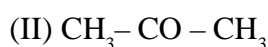
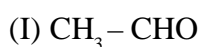
Q.10 Which of the following will give yellow precipitate with NaOH / I<sub>2</sub>



Q.11 Ethylmethanoate  $\xrightarrow[\text{(ii)H}_3\text{O}^+]{\text{(i)MeMgBr(2eq)}}$   $\xrightarrow{\text{W + X}}$  organic product



Which of the following organic product can be formed on dry distillation reaction



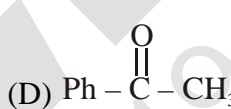
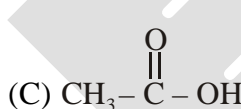
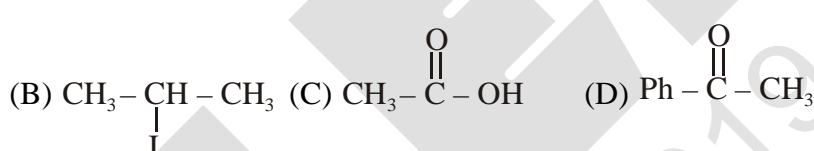
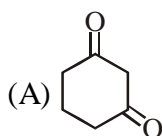
(A) I and II only

(B) II and III only

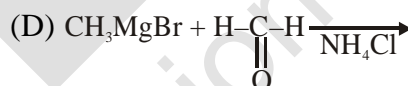
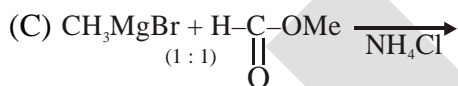
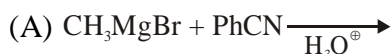
(C) I, II and IV only

(D) II and IV only

Q.12 Which of the following compounds(s) give a sweet smelling product having anesthetic use in presence of  $\text{Cl}_2$ , NaOH,  $\Delta$ .



Q.13 Reaction in which product can show positive haloform test :-



Q.14 In which reaction haloform is obtained as one product :-

(A) Electrolysis of ethanolic aqueous solution of NaCl

(B) Isopropanol with bleaching powder

(C) Chlorination of methane in sun light

(D) Chloral is treated with NaOH

Q.15. Fructose and glucose can be distinguished by :

[JEE-MAIN (APRIL)-2019]

(1) Fehling's test

(2) Barfoed's test

(3) Benedict's test

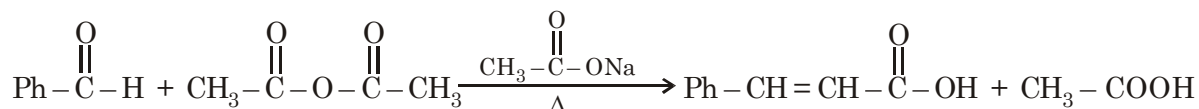
(4) Seliwanoff's test

### (5) PERKIN CONDENSATION

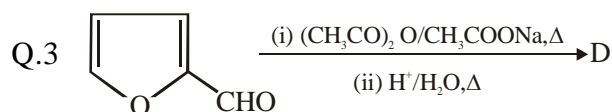
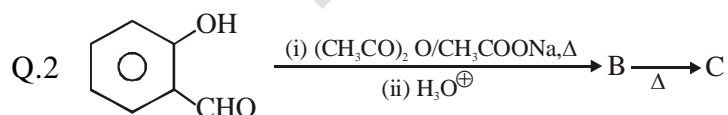
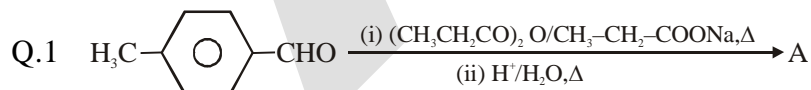
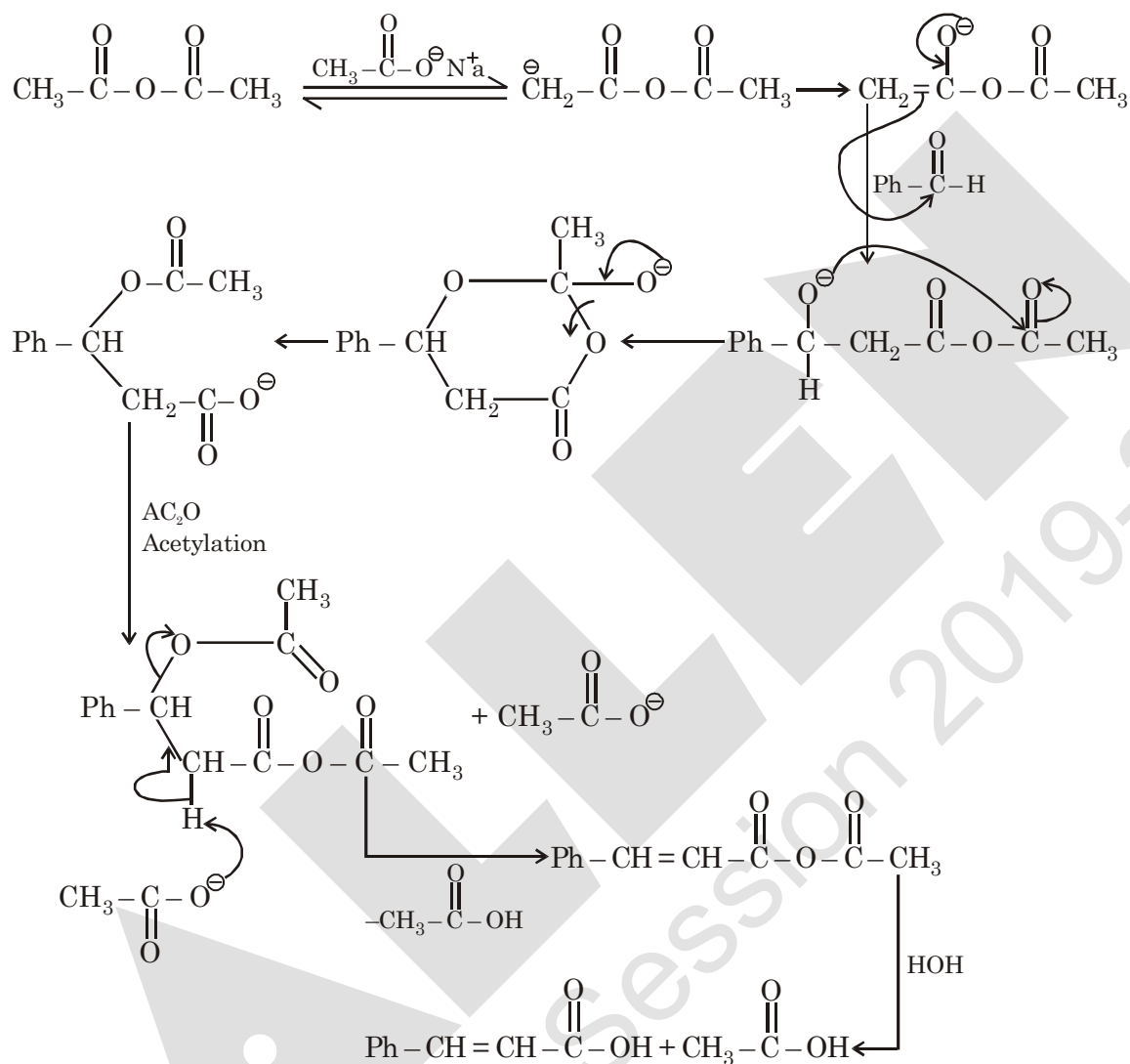
#### Perkin Reaction :

Condensation reaction between aromatic aldehyde and aliphatic acid anhydride having at least two alpha hydrogen in the presence of a base is known as **Perkin reaction**.

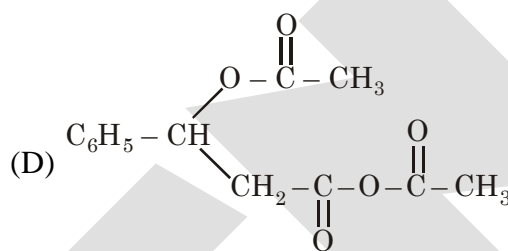
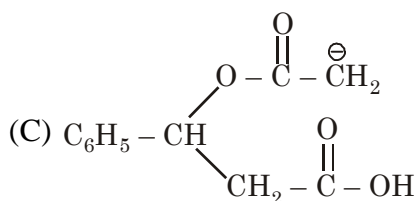
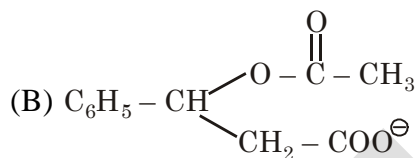
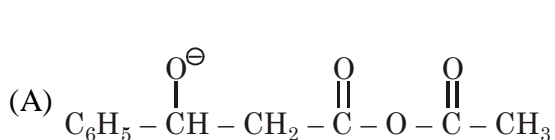
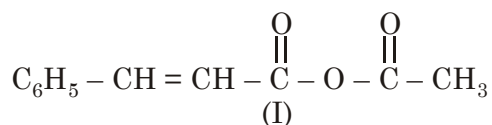
In this reaction, the anion of an acid anhydride adds to an aromatic aldehyde to produce an  $\beta$  aryl  $\alpha, \beta$ , unsaturated acid. In order to prevent side reactions, the base that is used to make the anion of the anhydride is usually the sodium salt of the acid corresponding to the anhydride.



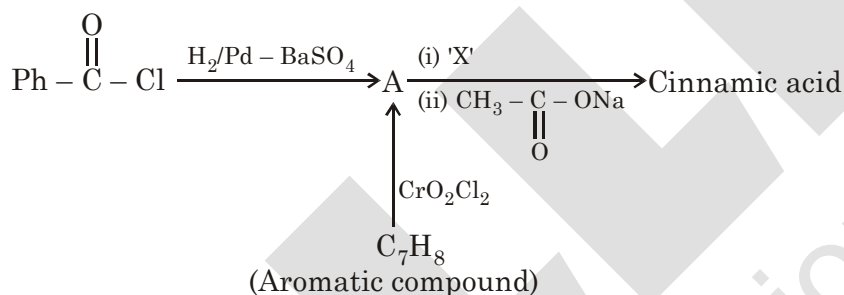
**Mechanism :**



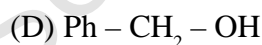
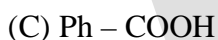
4. In the perkin reaction which one of the following intermediates gives compound (I)



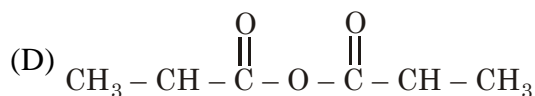
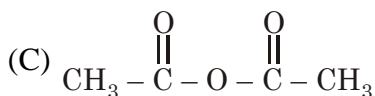
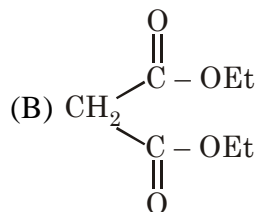
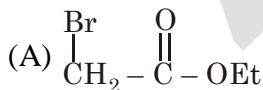
### Paragraph for Q.no. 5-6



5. Compound 'A' on treatment with conc. NaOH followed by acidification can give :



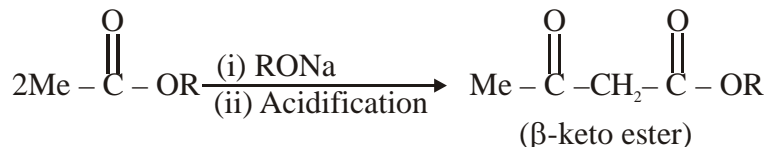
**6.** In the above reaction the reagent “X” can be :



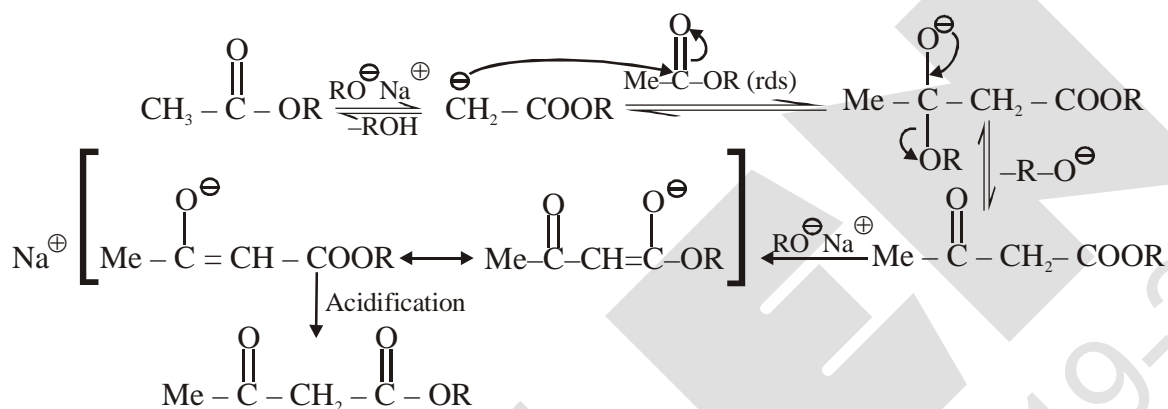


**(6) CLAISEN CONDENSATION**

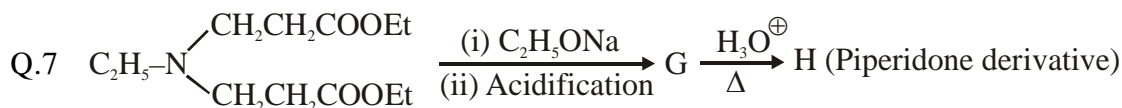
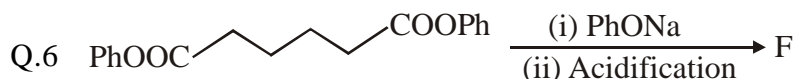
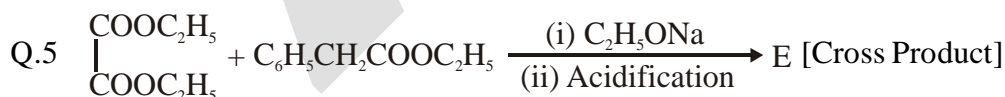
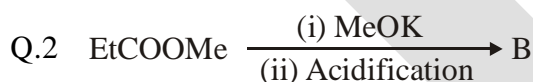
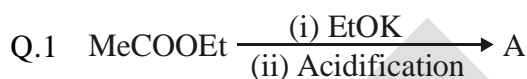
Esters undergo  $S_NAE$  Reaction, when attacked by a  $Nu^-$  generated by the interaction of a base (usually base related to the Alkoxy anion of ester) with one of the molecule of ester and this  $Nu^-$  attacks on another molecule. The reaction over all is considered as condensation of ester known as claisen ester condensation.



**Mechanism :**



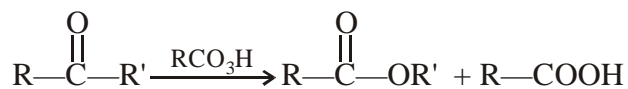
Some times, when two ester group are present within the molecule then the condensation occurs intramolecular then cyclization caused thus is known as Dieckmann cyclization or Dieckmann's condensation.



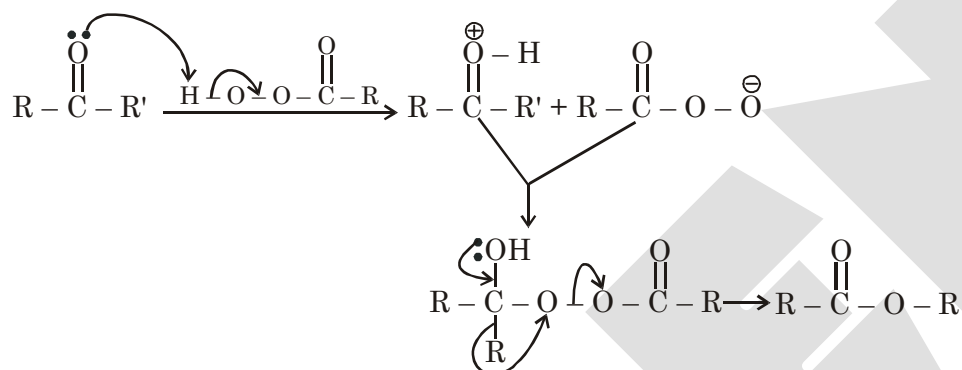
### (7) Beayer villiger oxidation

Reaction involve the oxidation of ketone to ester by treatment with per acid such as per acetic acid, MCPBA, per trifluoroacetic acid etc.

- It is a redox reaction
- Cyclic ketones are converted to lactone with ring expansion.

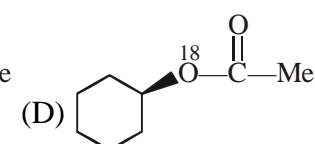
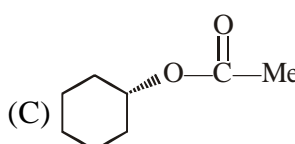
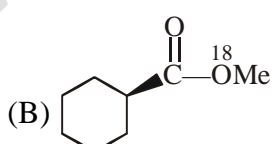
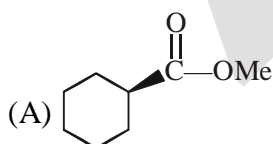
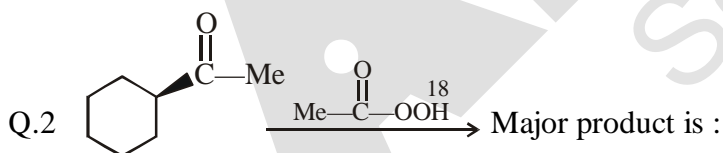
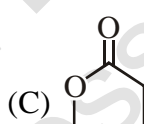
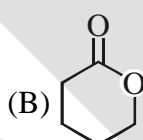
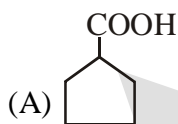
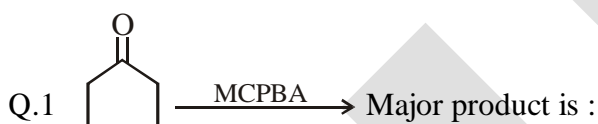
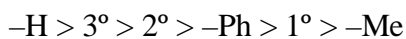


#### Mechanism



**Note :** In above reaction for shifting of groups migratory aptitude is applicable

Migratory order for above reaction



## ANSWER KEY

## (1) CANNIZARO REACTION

Q.1 Ans. (D)

As  $\text{Cl}_3\text{C}-\text{CHO}$  given chloroform

Q.2 Ans. (C)

In cromo cannizzaro reaction more reactive carbonyl compound is oxidised &amp; less in reduced.

Q.3 Ans. (B)

Intramolecular cannizzaro followed by heating effect

Q.4 Ans. (i)  $\text{CH}_3\text{OD} + \text{HCOONa}$ (ii)  $\text{DCH}_2\text{OD} + \text{DCOONa}$ Q.5 Ans. (i)  $\text{PhCH}_2\text{OD} + \text{PhCOONa}$ (ii)  $\text{Ph}-\text{CH}_2\text{OH} + \text{PhCOONa}^{18}$ Q.6 Ans. (i)  $\text{Ph}-\text{CH}_2\text{OH} + \text{HCOOK}$ (ii)  $\text{Ph}-\underset{\text{OH}}{\text{CH}}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{OK}$ Q.7 Ans. (i)  $\text{MeCH}_2-\text{CH}=\underset{\text{Me}}{\text{C}}-\overset{\text{O}}{\text{C}}-\text{H}$ (ii)  $\text{Me}_2\text{CH}-\text{CH}_2\text{OH} + \text{Me}_2\text{CHCOOK}$ Q.8 Ans. (i)  $\begin{array}{c} \text{OH} \quad \text{OH} \\ | \quad | \\ \text{---} \text{NO}_2 + \text{CH}_3\text{OH} \\ | \quad | \\ \text{HO} \quad \text{HCOOK} \end{array}$ (ii)  $\begin{array}{c} \text{OH} \quad \text{OH} \\ | \quad | \\ \text{---} \\ | \quad | \\ \text{HO} \quad \text{OH} \end{array} + \text{HCOOK}$ 

Q.9 Ans. (B)

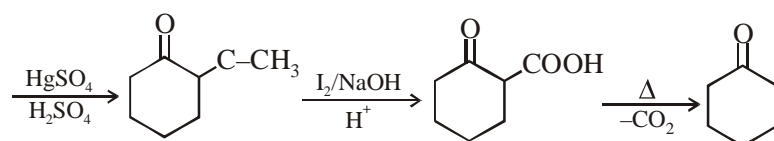
A :  $\text{Ph}-\overset{\text{O}}{\text{C}}-\text{CH}=\text{O}$     B :  $\text{Ph}-\underset{\text{H}}{\overset{\text{OH}}{\text{C}}}-\text{COO}^\ominus$     C :  $\text{Ph}-\underset{\text{OH}}{\text{CH}}-\text{COOH}$ 

Q.10 Ans. (A)→S ; (B)→P ; (C)→Q ; (D)→R

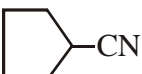
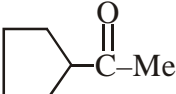
Q.11 Ans. (A)

A :  $\text{Ph}-\underset{\text{OH}}{\text{CH}}-\text{COONa}$     B :  $\text{PhCOOH}$     C : 

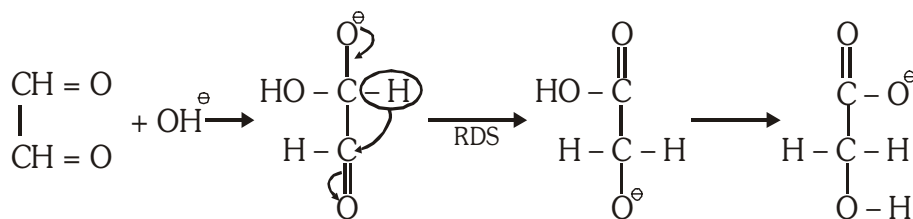
Q.12 Ans. (D)



Q.13 Ans. (B)

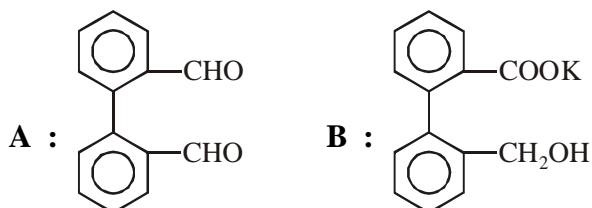
Q.14 Ans. (C) A : B : 

Q.15 Ans. (A)



option A is correct.

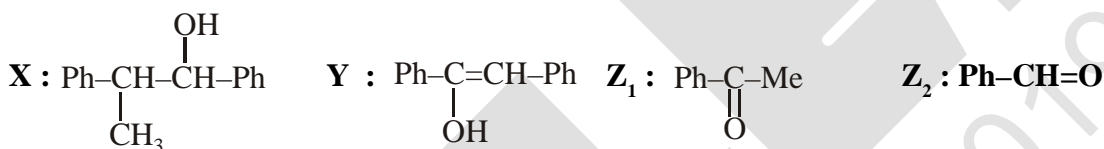
Q.16 Ans. (B)



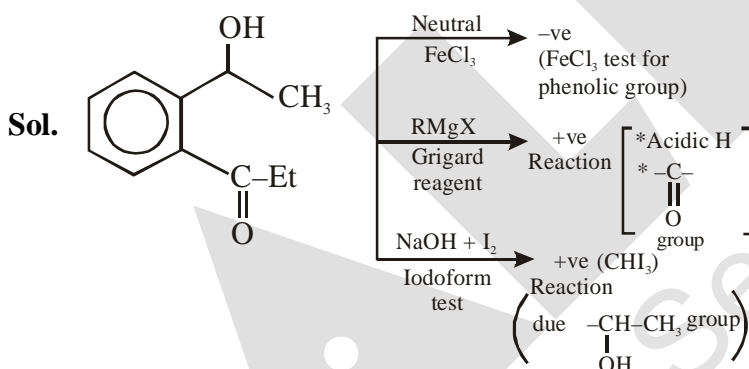
Q.17 Ans. (B)

Cron cannizaro reaction

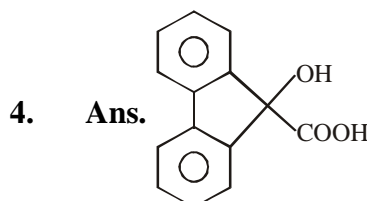
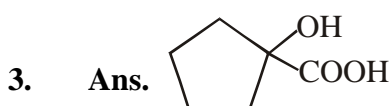
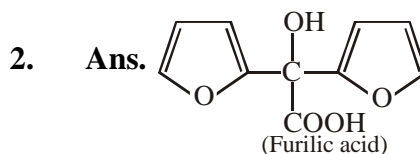
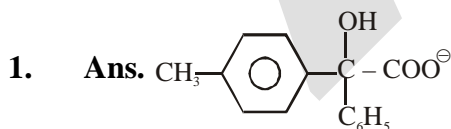
Q.18 Ans. (A)



Q.19 Ans. (1)

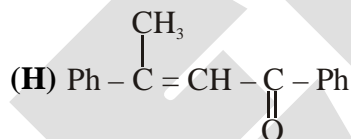
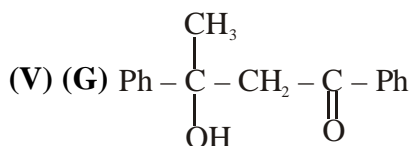
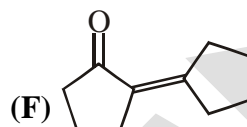
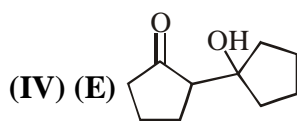
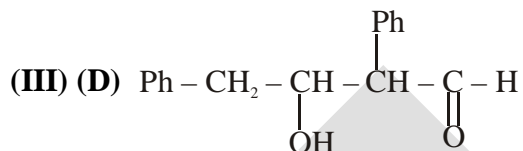
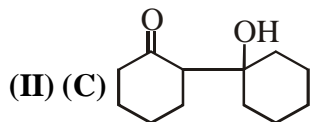
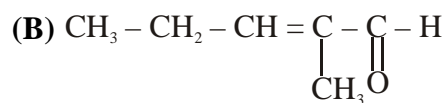
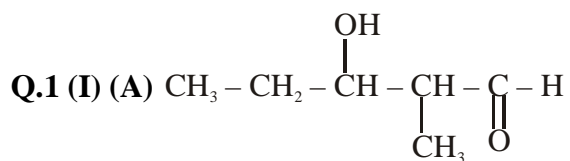


## (2) BENZIL-BENZILIC REARRANGEMENT OR BENZILIC ACID REARRANGEMENT

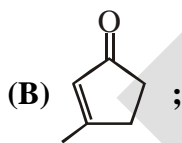
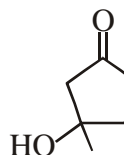


## (3) ALDOL CONDENSATION

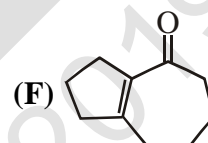
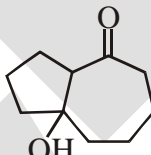
Q.1 Ans.



Q.2 Ans. (I) (A)



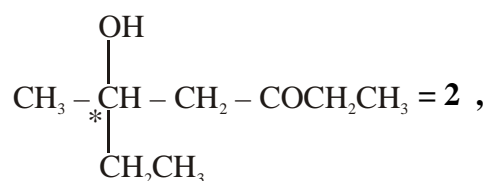
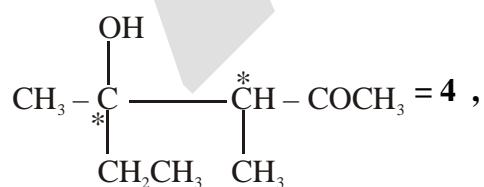
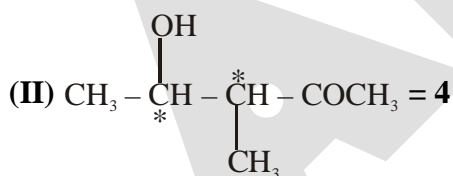
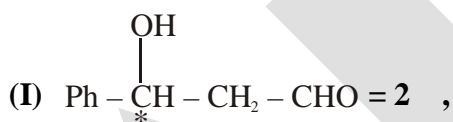
(II) (E)



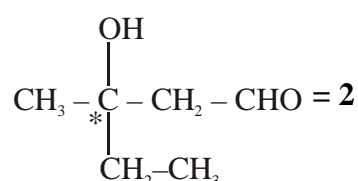
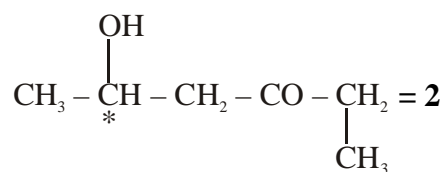
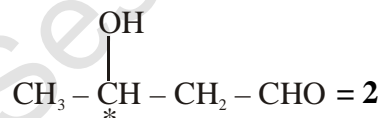
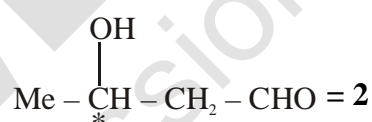
Q.3

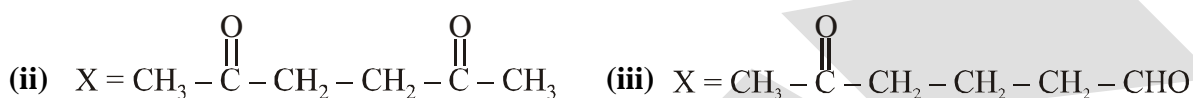
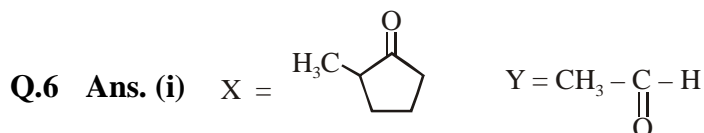
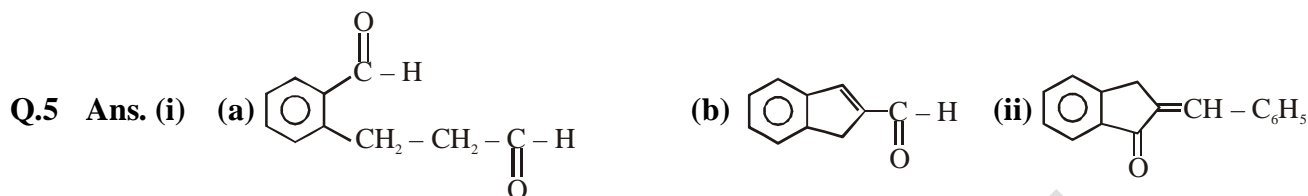
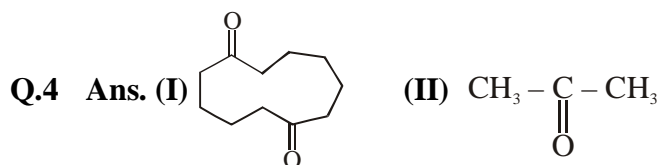
Ans.

Excluding Stereo



Including Stereo





Q.7 Ans. (C)

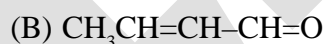
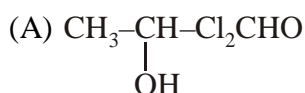
Intramolecular aldol condensation the 1,4-addition and finally Clemmensen reduction.

Q.8 Ans. (D)

Q.9 Ans. (B)

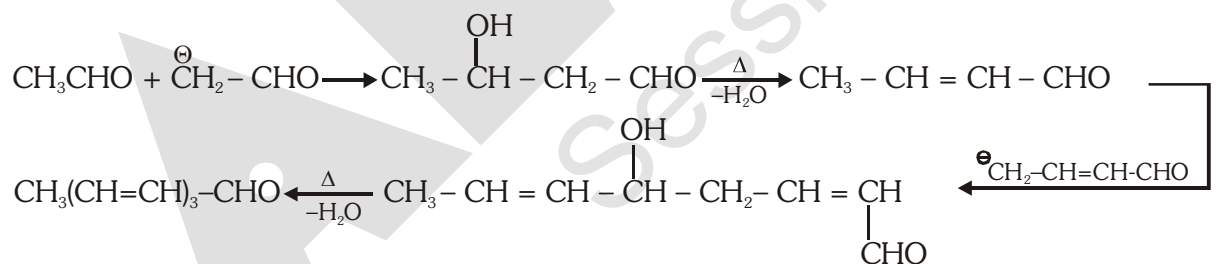
Ozonolysis followed by intramolecular aldol.

Q.10 Ans. (C)

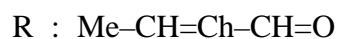
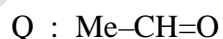
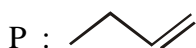


Q.11 Ans. (A)

Q.12 Ans. (A)



Q.13 Ans. (A)



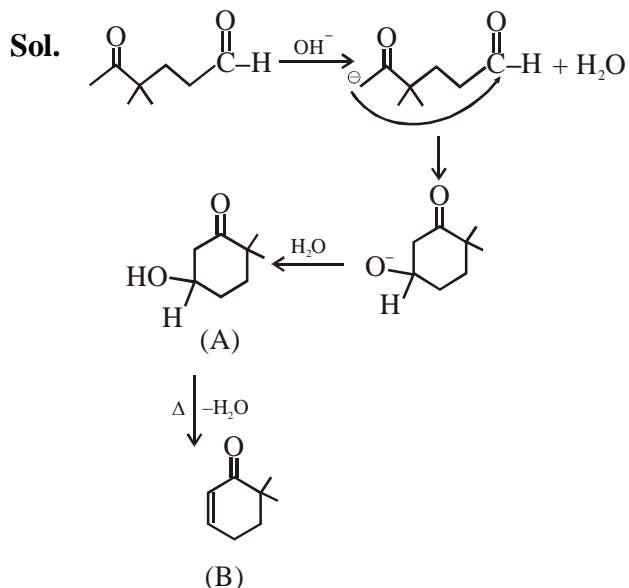
Q.14 Ans. (1)

Sol. Aldehyde reacts at a faster rate than ketone during aldol and sterically less hindered anion will be

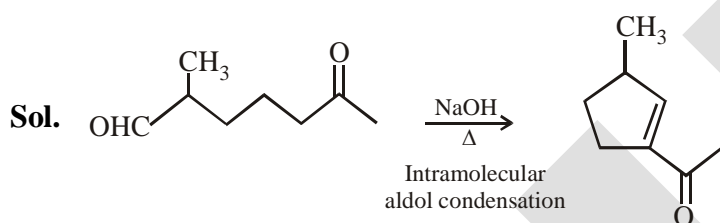
a better nucleophile so self aldol of  $\text{CH}_3 - \text{C}(=\text{O}) - \text{H}$  will be the major product.

Q.15 Ans. (4)

Q.16 Ans. (4)



Q.17 Ans. (4)

**(4) HALOGENATION OF THE  $\alpha$ -CARBON OF ALDEHYDES AND KETONES**

Q.1 Ans. (1, 2, 5, 7, 8, 9, 11)

Q.2 Ans. (i)  $\text{CH}_3\text{-COO}^- + \text{CHI}_3$ ; (ii)  $^- \text{O}-\text{C}(=\text{O})-\text{C}(=\text{O})-\text{O}^- + \text{CHI}_3$ ; (iii)  $\text{CH}_3\text{CH}_2\text{COO}^- + \text{CHI}_3$

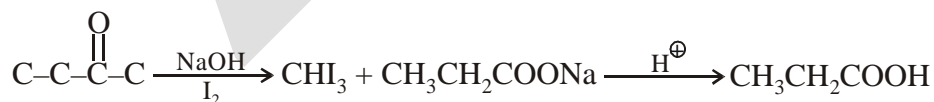
Q.3 Ans. (A,B,C)

Q.4 Ans. (C)

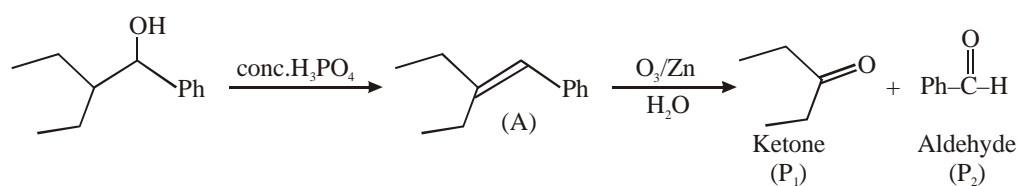


Q.5 Ans. (A)

Q.6 Ans. (A)

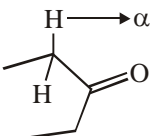


Q.7 Ans. (B)

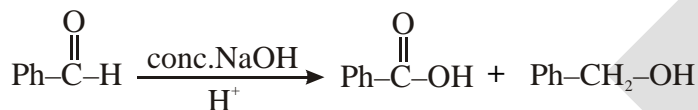


- (A) Both ketone & aldehyde react with braddy's reagent  $\text{H}_2\text{N}-\text{NH}-\text{C}_6\text{H}_3(\text{NO}_2)_2$  2, 4 dinitrophenyl hydrazine.
- (B) With  $\text{NaHSO}_3$  only aldehyde give crystalline bisulphite adduct whereas hindered ketone is unable react.
- (C)  $\text{NaHCO}_3$  will not react any of them.
- (D) Both  $\text{P}_1$  &  $\text{P}_2$  are unable to form idoform with  $\text{NaOH/I}_2$

**Q.8 Ans. (A)**

For aldol  $\alpha\text{H}$  should be present i.e.   $\text{P}_1$  where as  $\text{P}_2$   $\text{Ph}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$  will give cannizaro's as there is no.  $\alpha\text{H}$  in  $\text{P}_2$ .

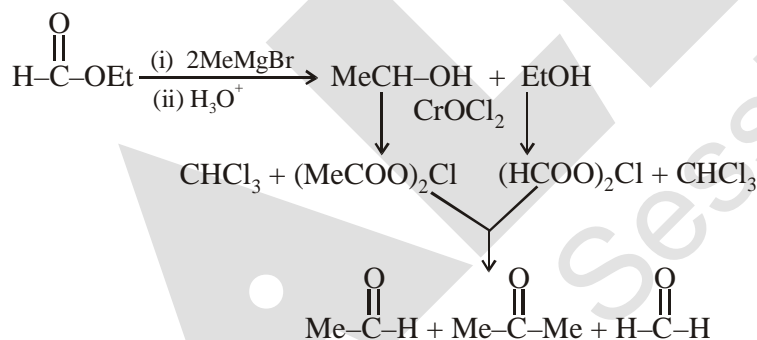
**Q.9 Ans. (D)**



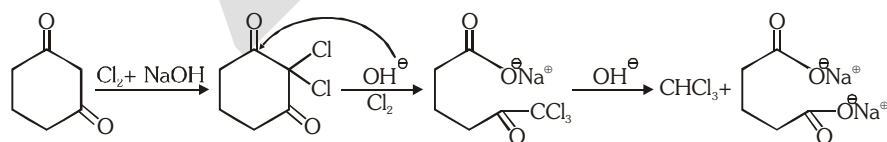
The above reaction is intermolecular redox reaction. In which desprotonation is taking place as a result of which 2 different products are formed from singlet reactant.

**Q.10 Ans. (A,B,C,D)**

**Q.11 Ans. (C)**



**Q.12 Ans. (A,B,D)**



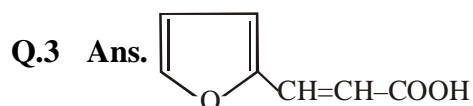
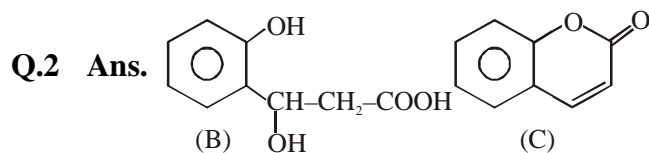
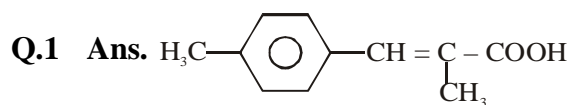
**Q.13 Ans. (A,B,C,D)**

**Q.14 Ans. (A,B,C,D)**

**Q.15. Ans. (4)**

Sol. Seliwanoff's test is used to distinguished aldose and ketose group.

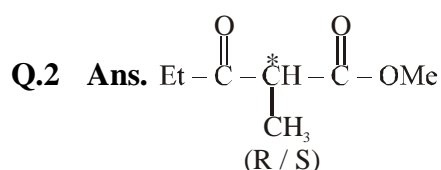
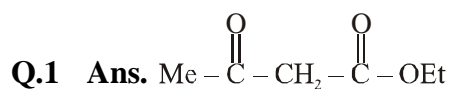


**(5) PERKIN CONDENSATION**

Q.4 Ans. (A)

Q.5 Ans. (C, D)

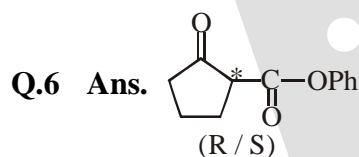
Q.6 Ans. (C)

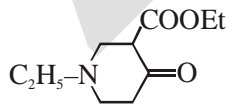
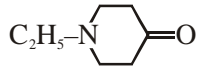
**(6) CLAISEN CONDENSATION**

Q.3 Ans. 4 products

Q.4 Ans.  $\text{C}_6\text{H}_5\text{COCH}_2\text{COOC}_2\text{H}_5$ ,  $\text{CH}_3\text{COCH}_2\text{COOC}_2\text{H}_5$   
Ethyl benzoylacetate

Q.5 Ans.  $\text{C}_6\text{H}_5-\text{CH}(\text{COOC}_2\text{H}_5)_2$   
Diethyl- $\alpha$ -oxalophenyl acetate



Q.7 Ans. (G) , (H)   
1-Ethyl-4-piperidone

**(7) Beayer villiger oxidation**

Q.1 Ans. (B)

Q.2. Ans. (D)

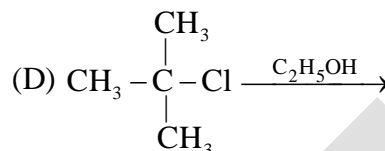
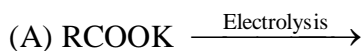
**ALLEN**  
Session 2019-20

**ALLEN**  
Session 2019-20

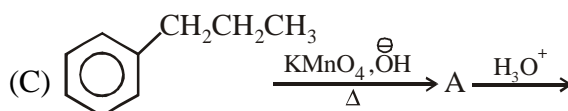
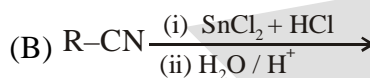
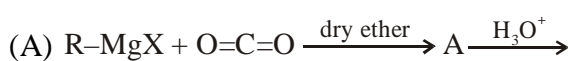
**CARBOXYLIC ACIDS AND IT'S DERIVATIVE, ALIPHATIC AMINES**

**EXERCISE # I**

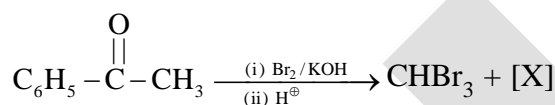
1. In which reaction product is hydrocarbon ?



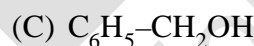
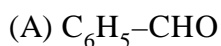
2. Which of the following set of reaction can not prepare carboxylic acid as the final product :



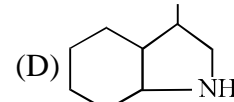
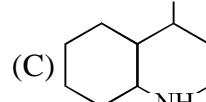
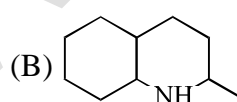
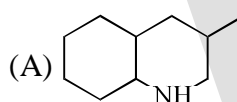
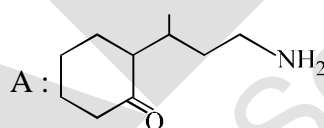
3. In the given reaction,



[X] will be :



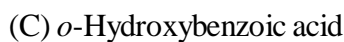
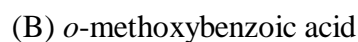
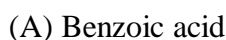
4. Reductive amination of A forms:



5. In the given reaction :

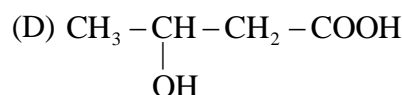
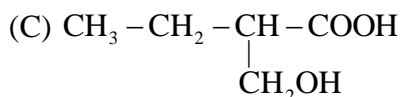
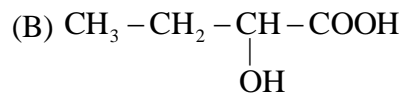
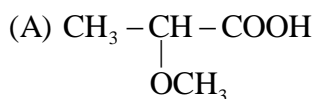


[X] will be :





10. Which optically active compound on reduction with  $\text{LiAlH}_4$  will give optically inactive compound?



11. Which will form lactone on treatment with  $\text{NaOH}$ ?

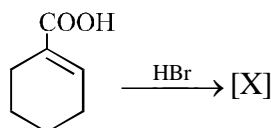
(A)  $\alpha$ -Bromo acid

(B)  $\beta$ -Bromo acid

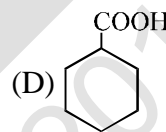
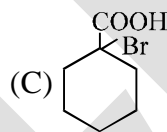
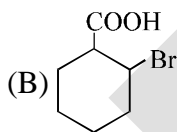
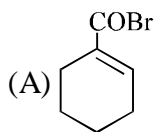
(C)  $\beta$ -Hydroxy acid

(D)  $\delta$ -Bromo acid

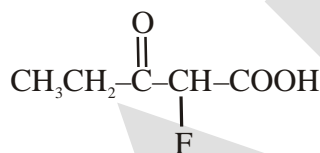
12. In the given reaction:



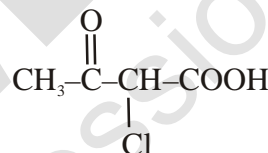
[X] will be :



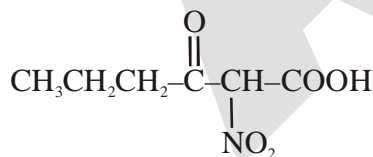
13. Correct order of decarboxylation



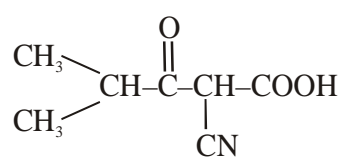
(a)



(b)



(c)



(d)

(A)  $a > b > c > d$

(B)  $c > d > b > a$

(C)  $c > d > a > b$

(D)  $d > c > a > b$

14. N-Ethyl phthalimide on hydrolysis gives:

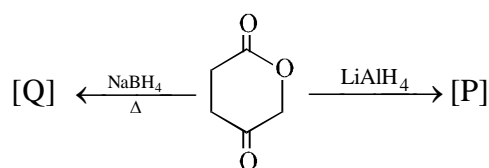
(A) Methyl alcohol

(B) Ethyl amine

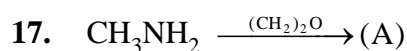
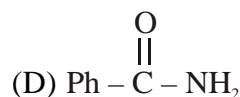
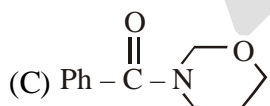
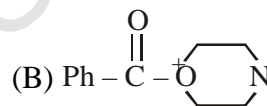
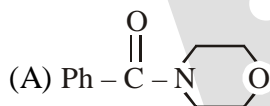
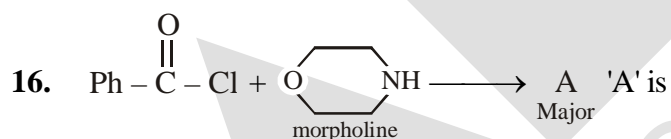
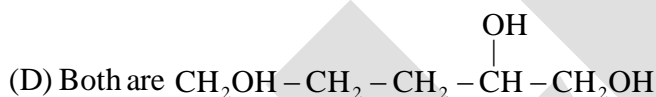
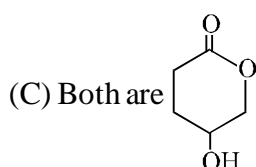
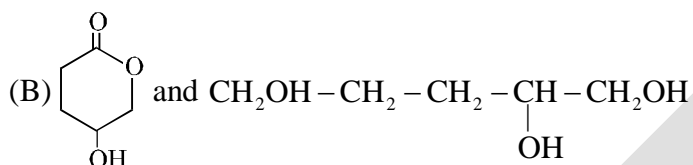
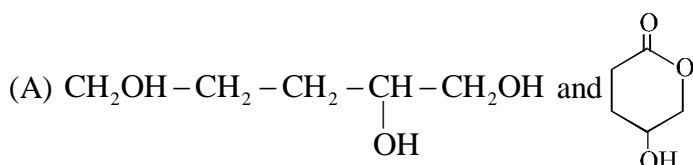
(C) Dimethyl amine

(D) Diethyl amine

15. In the given reaction:



[P] and [Q] respectively be :



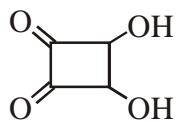
(A) 'A' is more basic than  $\text{CH}_3\text{NH}_2$

(B) 'A' is less basic than  $\text{CH}_3\text{NH}_2$

(C) 'A' is Ter-amine

(D) None

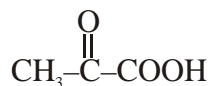
18. Which of the following can released  $\text{CO}_2$  with  $\text{NaHCO}_3$ .



(i)



(ii)



(iii)

(A) (i), (ii) & (iii)

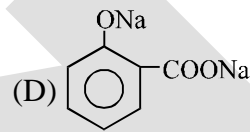
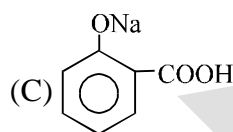
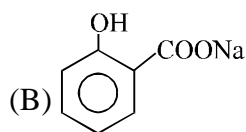
(B) (i) & (ii)

(C) (ii) & (iii)

(D) (i) & (ii)

19. Sodium bicarbonate reacts with salicylic acid to form :

(A)  $\text{C}_6\text{H}_5\text{ONa}$



20. Which of the following diazonium salt is relatively stable at  $0-5^\circ\text{C}$ :

(A)  $\text{CH}_3-\text{N}\equiv\text{N}\}^+\text{Cl}^-$

(B)  $(\text{CH}_3)_2\text{CH}-\text{N}\equiv\text{N}\}^+\text{Cl}^-$

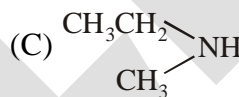
(C)  $\text{C}_6\text{H}_5-\text{N}\equiv\text{N}\}^+\text{Cl}^-$

(D)  $(\text{CH}_3)_3\text{C}-\text{N}\equiv\text{N}\}^+\text{Cl}^-$

21. Which is most volatile ?

(A)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$

(B)  $(\text{CH}_3)_3\text{N}$



(D)  $\text{CH}_3\text{OH}$

22.  $\text{C}_6\text{H}_5\text{CONH}_2 \xrightarrow{\text{Br}_2/\text{OD}^\ominus} \text{P}$ , 'P' is :

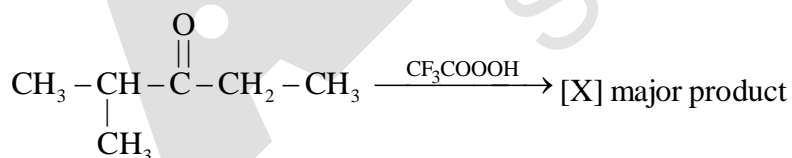
(A)  $\text{C}_6\text{H}_5\text{COND}_2$

(B)  $\text{C}_6\text{H}_5\text{ND}_2$

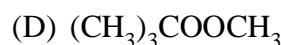
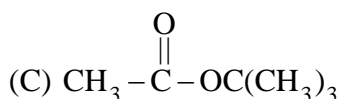
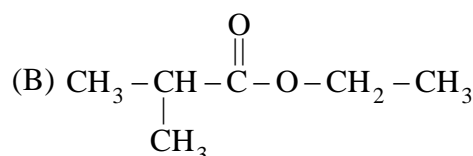
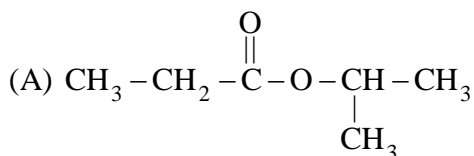
(C)  $\text{C}_6\text{H}_5\text{NHD}$

(D)  $\text{C}_6\text{H}_5\text{NH}_2$

23. In the given reaction:

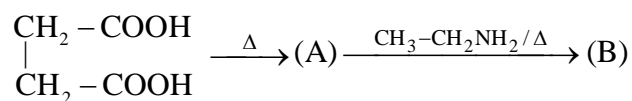


[X] will be:

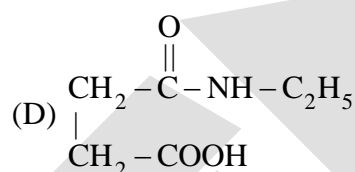
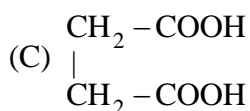
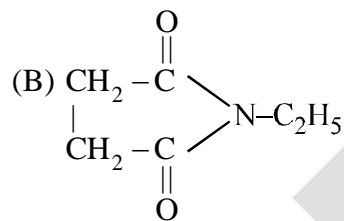
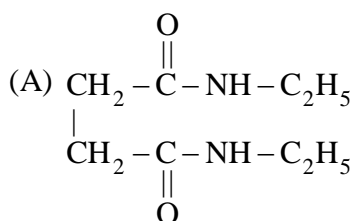




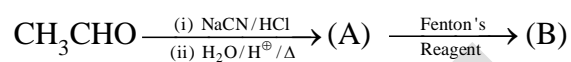
24. In the given reaction sequence:



(B) will be:



25. In the given reaction :



(B) will be :

(A) Acetic acid

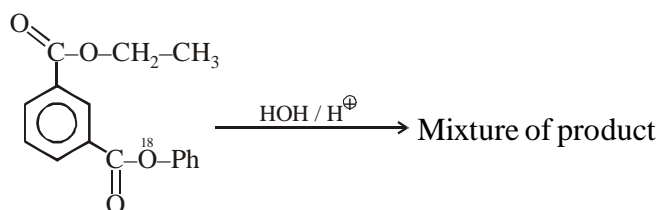
(B) Oxalic acid

(C) Pyruvic acid

(D) Citric acid

EXERCISE # II

1. Which of the following is/are present in mixture of product :



- (A)  $\text{CH}_3\text{-CH}_2\text{-OH}$  (B) (C)  $\text{Ph-}^{18}\text{OH}$  (D)

2. Mixture of  $1^\circ$ ,  $2^\circ$  and  $3^\circ$  amines can be separated by:

- (A) Hinsberg's method (B) Hofmann's isocyanide test  
(C) Fractional distillation (D)  $\text{NaNO}_2/\text{HCl}$

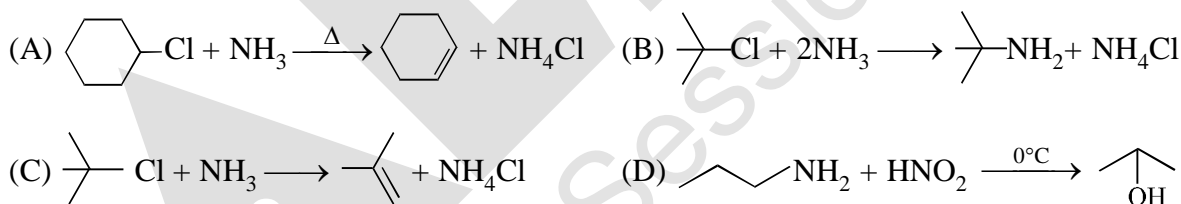
3.  $\text{RCOOR}'$  can be prepared by:

- (A) Esterification of  $\text{RCOOH}$   
(B) Reaction of  $\text{CH}_3\text{CH=CH}_2$  with methanol  
(C) Baeyer-Villiger oxidation of  $\text{RCOR}'$  with peroxy acid  
(D) reaction of  $\text{RCOCl}$  with  $\text{R}'\text{OH}$

4. Which of the following amine reacts with Hinsberg reagent to give base soluble product :-

- (A) Neopentyl amine (B) sec propyl amine (C) diethyl amine (D) ethyl methyl amine

5. Which is/are correct reaction(s):



6. Which of the following will form acetyl chloride with  $\text{PCl}_5$ ?

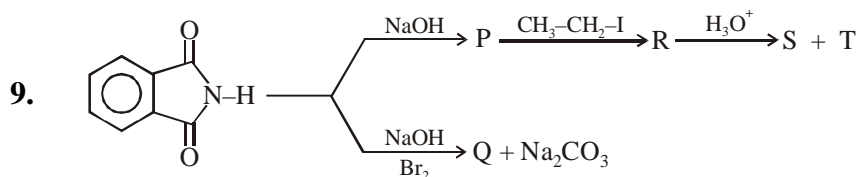
- (A)  $\text{MeCOOH}$  (B)  $\text{MeCOOMe}$  (C)  $\text{MeCOOCOMe}$  (D)  $\text{Me-CONH}_2$

7. Sodium salt of which compound on electrolysis does not give hydrocarbon:

- (A)  $\text{C}_6\text{H}_5\text{COOH}$  (B)  $\text{HCOOH}$  (C)  $\text{Me}_3\text{C-COOH}$  (D)  $\text{COOH-CH=CH-COOH}$

8. Among the following, which statement is not correct ?

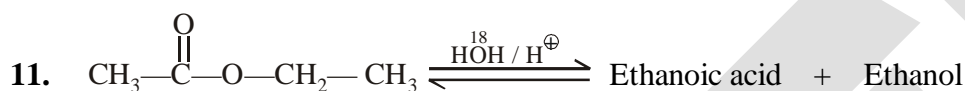
- (A)  $\text{H}_3\text{C-C(=O)-OH}$  will not respond to haloform test  
(B) Schiff's reagent and Schiff's base are different compounds  
(C) Fehling's solution is a good reagent to detect aromatic aldehydes  
(D) Both aldehyde and ketone can react with 2,4-dinitrophenylhydrazine reagent



If T can evolve effervescence of  $\text{CO}_2$  with a  $\text{NaHCO}_3$ , then correct statement(s) is/are :

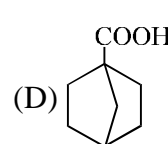
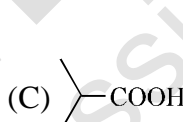
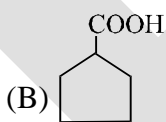
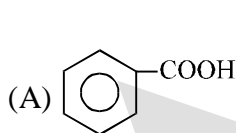
- (A) S & Q can be distinguished by dye azo test  
 (B) T is most acidic among all isomeric benzenoid dicarboxylic acid  
 (C) Q & S can be distinguished by mustered oil test  
 (D) P, Q & T all are soluble in a  $\text{NaHCO}_3$
10. Acetic anhydride and ammonia gives the product:

- (A)  $\text{CH}_3\text{CONH}_2$  (B)  $\text{CH}_3\text{CONHCH}_3$  (C)  $\text{CH}_3\text{CN}$  (D)  $\text{CH}_3\text{COONH}_4$



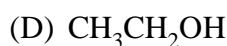
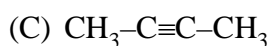
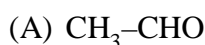
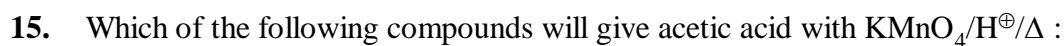
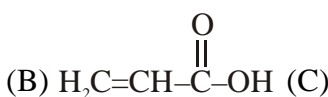
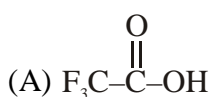
Isotopic oxygen of water will be present with

- (A) Ethanoic acid  
 (B) Ethanol  
 (C) After some time it will also be present in some molecules of ester  
 (D) None of these
12. Which one of the following compounds will give HVZ reaction?



Rate of reaction will be faster if 'R' is

- (A)  $\text{CH}_3-$  (B)  $\text{C}_2\text{H}_5-$  (C)  $\text{NO}_2-$  (D)  $\text{CN}-$
14. Which of the following carboxylic acids do not undergo decarboxylation simply on heating ?



16. Hofmann degradation is given by:

- (A) Succinimide (B) Acid chloride (C) Acid anhydride (D) Acetamide

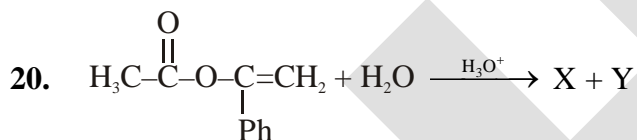
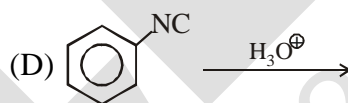
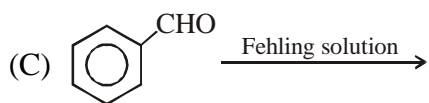
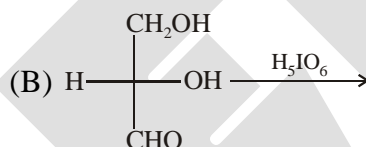
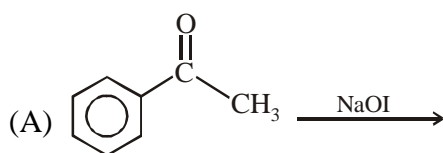
17. The presence of primary amine can be confirmed by its reaction with :

- (A)  $\text{HNO}_2$  (B)  $\text{CHCl}_3 + \text{NaOH}$  (C)  $\text{CS}_2$  &  $\text{HgCl}_2$  (D)  $\text{H}_2\text{SO}_4$

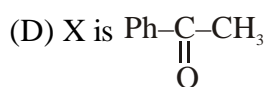
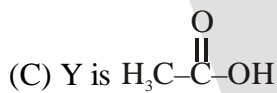
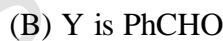
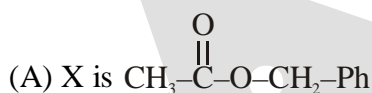
18. Total number of compounds which are soluble in hot a NaOH are :

- (i) Salicyclic acid (ii) Aspirine (iii) Carbolic acid (iv) Acetic acid  
(v) Succinic anhydride (vi) Cyclohexanone (vii) Benzene sulphonamide (viii) Cyclohexene  
(A) 5 (B) 6 (C) 7 (D) 8

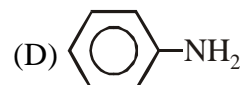
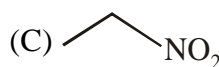
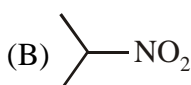
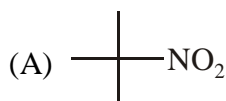
19. Number of oxidation reactions in which organic reactant gets oxidised & one of the major product is carboxylic acid/salt :



X and Y are :



21. Which of the following compound react with  $\text{HNO}_2$  :



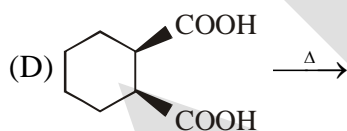
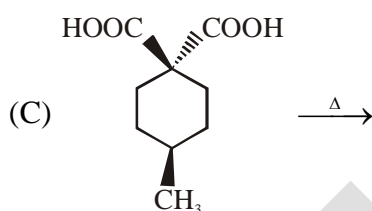
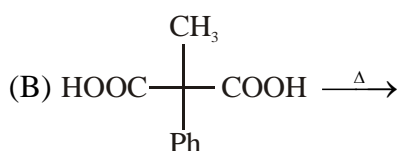
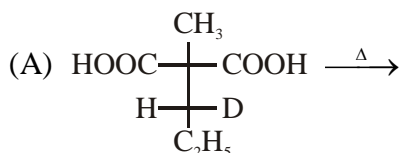
## EXERCISE # III

## Matching Type Questions

1. Match the following question :

## Column - I

(Reaction)



## Column-II

(Products)

(P) Diastereomers

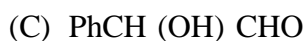
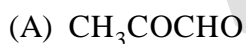
(Q) Racemic mixture

(R) Meso comp.

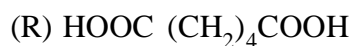
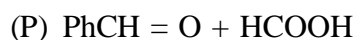
(S)  $\text{CO}_2$  gas will evolve

2. Match the following question :

## Column I

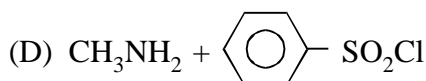
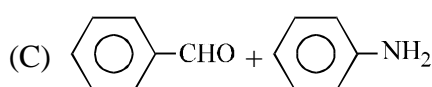
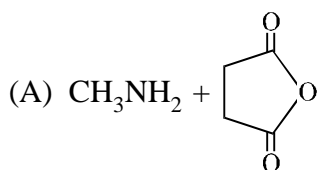
(Organic compounds oxidised by  $\text{HIO}_4$ )

## Column II

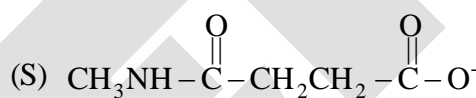
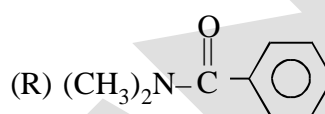
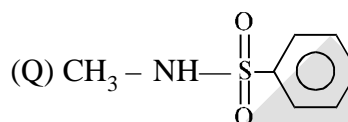
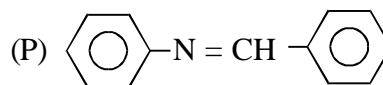
(Products of  $\text{HIO}_4$  oxidation)

3. Match the following question :

Column I (Reactions)



Column II (Products)



4. Match the following question :

Column I

(Correct about product)



Column II

(P) Product is yellow oily liquid

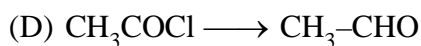
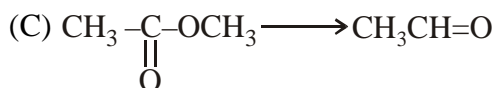
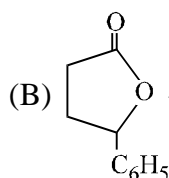
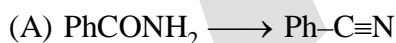
(Q) Gives red colour with CAN

(R) Gives fruity smell with  $\text{CH}_3\text{OH}$

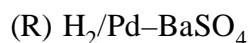
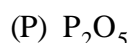
(S) Foul smelling compound is formed.

5. Match the following question :

Column I

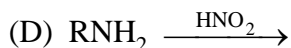
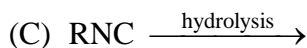
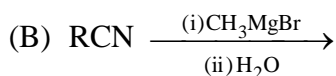
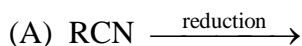


Column II



6. Match the following question :

**Column I**



**Column II**

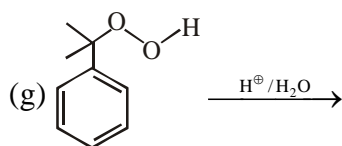
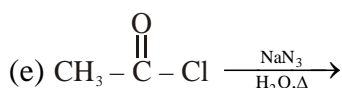
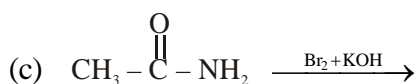
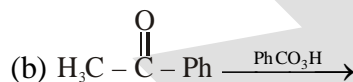
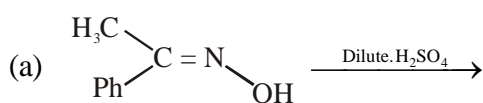
(P) 1° Amine

(Q) Alcohol

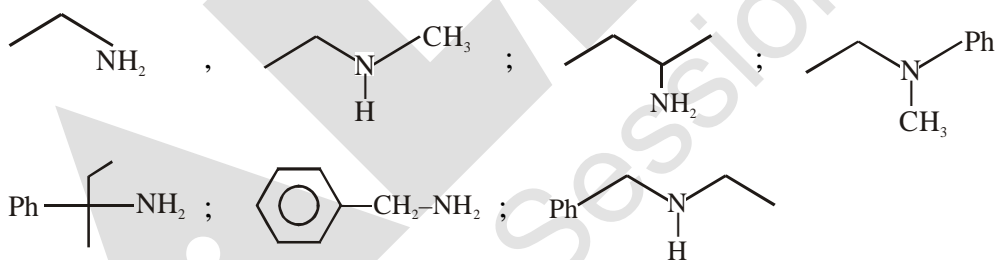
(R) Ketone

(S) Acid

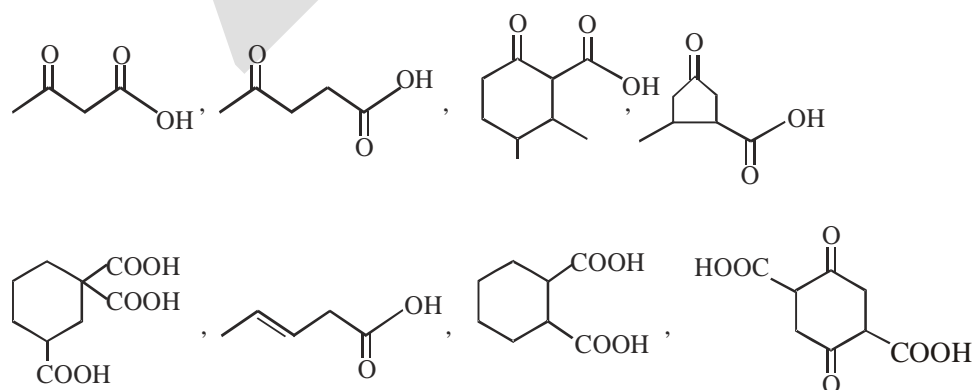
7. Find out number of reactions which involve electron deficient nitrogen [Nitrene character] during reaction mechanism.

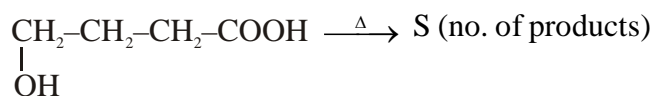
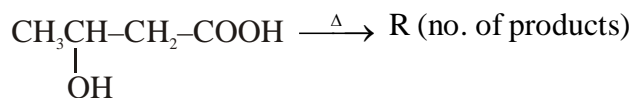
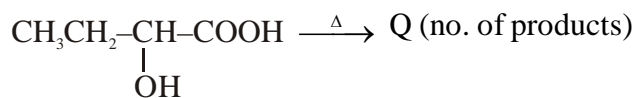
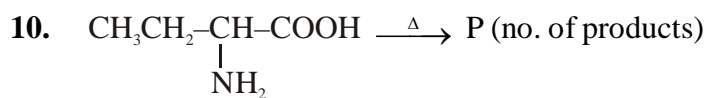


8. Of the following amines how many can be separated by Hoffmann's mustard oil reaction.



9. Examine the structure of following compounds, and find out number of compounds that will undergo decarboxylation in presence of heat.





In all reactions the sum of product is.

**How will you bring about the following transformation:**

11. Propanoic acid into lactic acid.
12. Ethyl benzene to 2-phenyl propionic acid.
13. Acetamide from acetone.



## EXERCISE # IV (A) (JEE-MAIN)

1. Reaction -

[AIEEE-2002]

Primary amine +  $\text{CHCl}_3 + \text{KOH} \rightarrow$  product, here product will be -

- (1) Cyanide                      (2) Isocyanide                      (3) Amine                      (4) Alcohol

2. The compound formed in the positive test for nitrogen with the Lassaigne solution of an organic compound is-

[AIEEE-2004]

- (1)  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$                       (2)  $\text{Na}_3[\text{Fe}(\text{CN})_6]$                       (3)  $\text{Fe}(\text{CN})_3$                       (4)  $\text{Na}_4[\text{Fe}(\text{CN})_5]\text{NOS}$

3. Which one of the following methods is neither meant for the synthesis nor for separation of amines-

- (1) Hofmann method                      (2) Hinsberg method                      [AIEEE-2005]  
(3) Curtius reaction                      (4) Wurtz reaction

4. In the chemical reaction,  $\text{CH}_3\text{CH}_2\text{NH}_2 + \text{CHCl}_3 + 3\text{KOH} \rightarrow (\text{A}) + (\text{B}) + 3\text{H}_2\text{O}$ , the compounds (A) and (B) are respectively -

[AIEEE-2007]

- (1)  $\text{C}_2\text{H}_5\text{CN}$  and  $3\text{KCl}$                       (2)  $\text{CH}_3\text{CH}_2\text{CONH}_2$  and  $3\text{KCl}$   
(3)  $\text{C}_2\text{H}_5\text{NC}$  and  $\text{K}_2\text{CO}_3$                       (4)  $\text{C}_2\text{H}_5\text{NC}$  and  $3\text{KCl}$

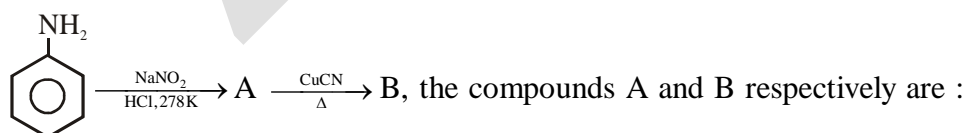
5. In the chemical reactions,

[AIEEE-2010]



- (1) Nitrobenzene and chlorobenzene  
(2) Nitrobenzene and fluorobenzene  
(3) Phenol and benzene  
(4) Benzene diazonium chloride and fluorobenzene

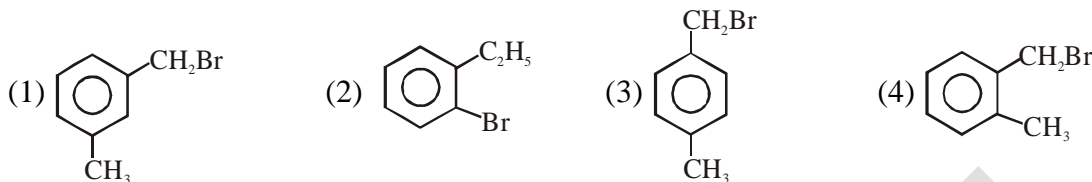
6. In the chemical reactions



[AIEEE-2011]

- (1) Fluorobenzene and phenol                      (2) Benzene diazonium chloride and benzonitrile  
(3) Nitrobenzene and chlorobenzene                      (4) Phenol and bromobenzene

7. Compound (A),  $C_8H_9Br$ , gives a white precipitate when warmed with alcoholic  $AgNO_3$ . Oxidation of (A) gives an acid (B),  $C_8H_6O_4$ . (B) easily forms anhydride on heating. Identify the compound (A): [AIEEE-2013]



8. An organic compound A upon reacting with  $NH_3$  gives B. On heating, B gives C. C in presence of  $KOH$  reacts with  $Br_2$  to give  $CH_3CH_2NH_2$ . A is :- [AIEEE-2013]

- (1)  $CH_3COOH$  (2)  $CH_3CH_2CH_2COOH$   
 (3)  $CH_3-CH(CH_3)-COOH$  (4)  $CH_3CH_2COOH$

9. On heating an aliphatic primary amine with chloroform & ethenolic potassium hydroxide the organic compound formed is [AIEEE-2014]

- (1) An alkyl cyanide (2) An alkyl isocyanide  
 (3) an alkanol (4) an alkanediol

10. In the reaction  $CH_3COOH \xrightarrow{LiAlH_4} A \xrightarrow{PCl_5} B \xrightarrow{alc.KOH} C$  'C' is [AIEEE-2014]

- (1) Ethylene (2) Acetyl chloride (3) Acetaldehyde (4) Acetylene.

11. In the presence of a small amount of phosphorous, aliphatic carboxylic acids react with chlorine or bromine to yield a compound in which  $\alpha$  - hydrogen has been replaced by halogen. This reaction is known as : [JEE(Main)-2015]

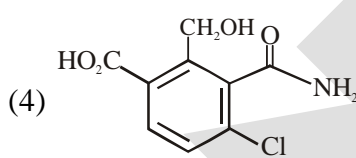
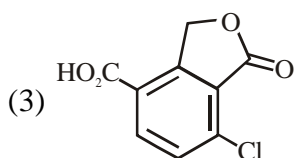
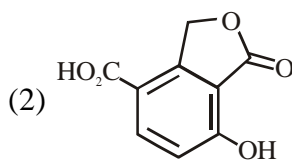
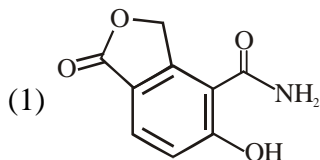
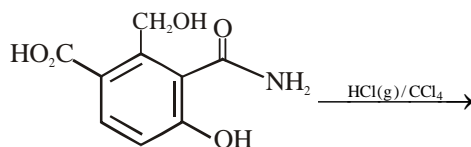
- (1) Etard reaction (2) Hell - Volhard - Zelinsky reaction  
 (3) Wolff - Kischner reaction (4) Rosenmund reaction

12. In the Hofmann bromamide degradation reaction, the number of moles of  $NaOH$  and  $Br_2$  used per mole of amine produced are : [JEE(Main)-2016]

- (1) Four moles of  $NaOH$  and one mole of  $Br_2$   
 (2) One mole of  $NaOH$  and one mole of  $Br_2$   
 (3) Four moles of  $NaOH$  and two moles of  $Br_2$   
 (4) Two moles of  $NaOH$  and two moles of  $Br_2$

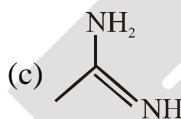
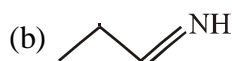
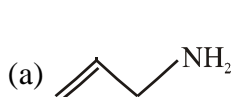
13. The major product expected from the following reaction is :

[JEE(Main On-Line)-2017]



14. The increasing order of basicity of the following compounds is :

[JEE(Main)-2018]



(1) (b) < (a) < (c) < (d)

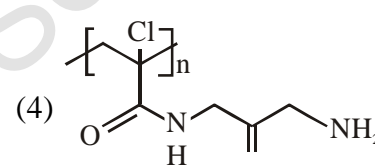
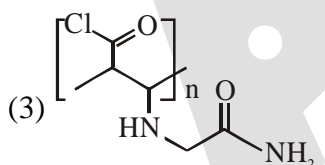
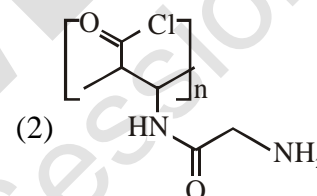
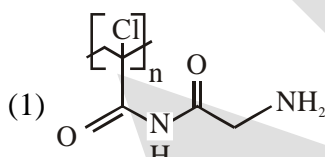
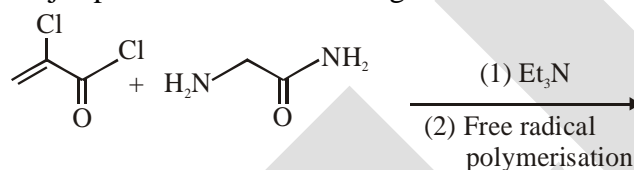
(2) (b) < (a) < (d) < (c)

(3) (d) < (b) < (a) < (c)

(4) (a) < (b) < (c) < (d)

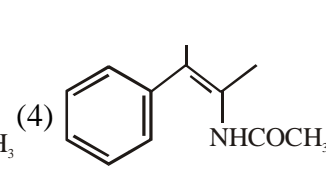
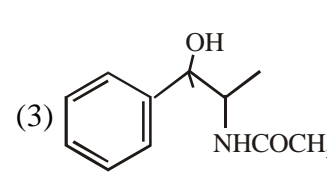
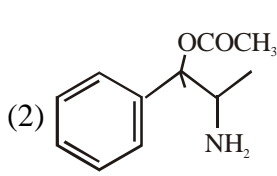
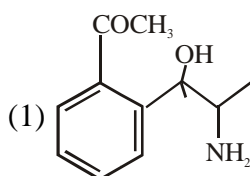
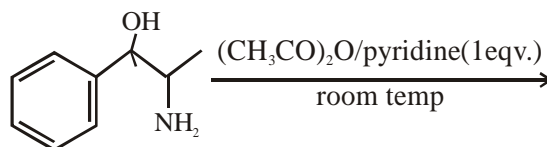
15. Major product of the following reaction is :

[JEE Main (Jan)-2019]



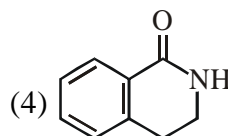
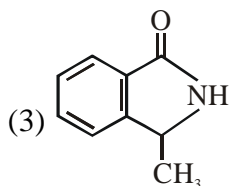
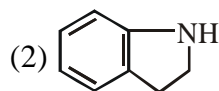
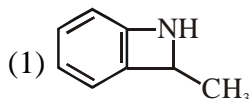
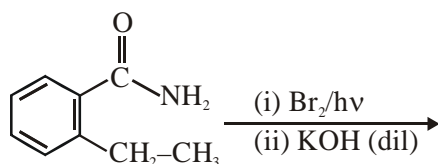
16. The major product obtained in the following reaction is :

[JEE Main (Jan)-2019]



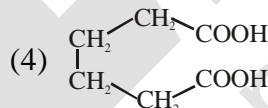
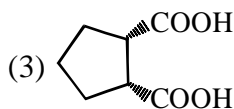
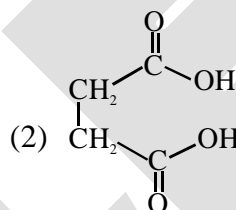
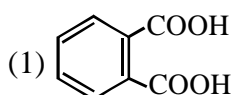
17. The major product of the following reaction is :

[JEE Main (Jan)-2019]

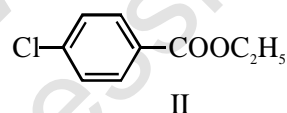
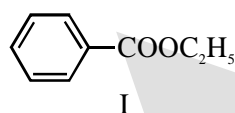


18. Which dicarboxylic acid in presence of a dehydrating agent is least reactive to give an anhydride :

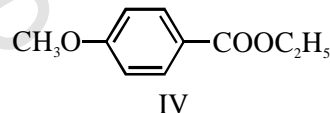
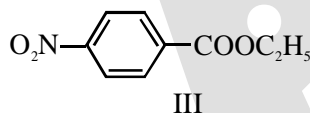
[JEE Main (Jan)-2019]



19. The decreasing order of ease of alkaline hydrolysis for the following esters is :



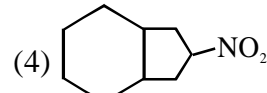
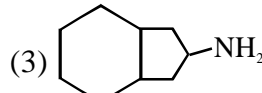
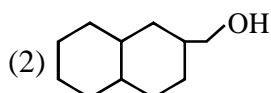
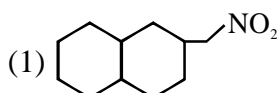
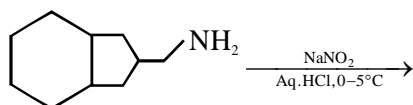
[JEE Main (Jan)-2019]



- (1) IV > II > III > I    (2) III > II > I > IV    (3) III > II > IV > I    (4) II > III > I > IV

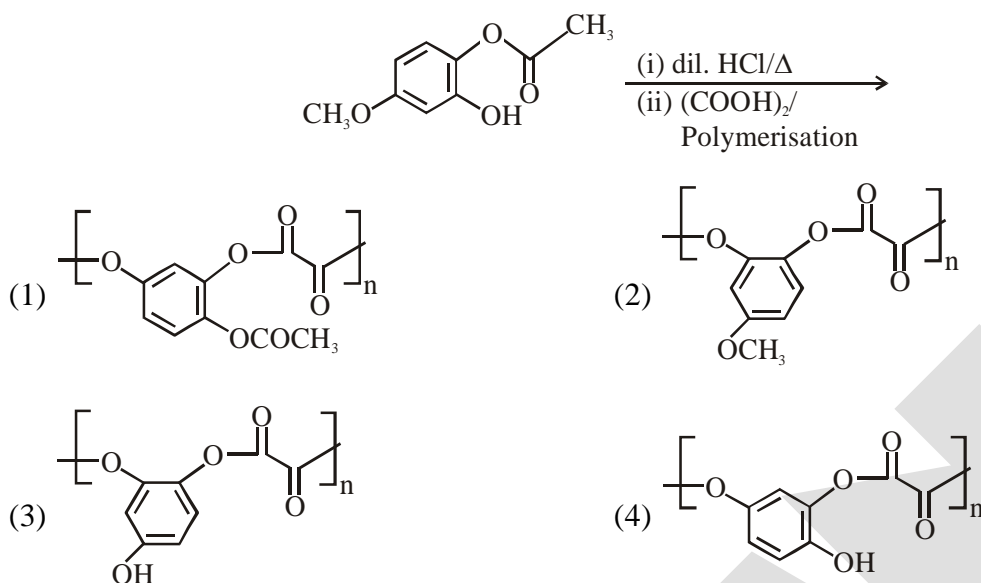
20. The major product formed in the reaction given below will be :

[JEE Main (Jan)-2019]



21. The major product of the following reaction is:

[JEE Main (Jan)-2019]



22. An aromatic compound 'A' having molecular formula  $C_7H_6O_2$  on treating with aqueous ammonia and heating forms compound 'B'. The compound 'B' on reaction with molecular bromine and potassium hydroxide provides compound 'C' having molecular formula  $C_6H_7N$ . The structure of 'A' is :

[JEE Main (Jan)-2019]



23. A compound 'X' on treatment with  $Br_2/NaOH$ , provided  $C_3H_9N$ , which gives positive carbylamine test. Compound 'X' is :-

[JEE Main (Jan)-2019]

- (1)  $CH_3COCH_2NHCH_3$  (2)  $CH_3CH_2COCH_2NH_2$   
 (3)  $CH_3CH_2CH_2CONH_2$  (4)  $CH_3CON(CH_3)_2$

24. The increasing order of reactivity of the following compounds towards reaction with alkyl halides directly is :

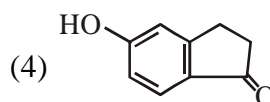
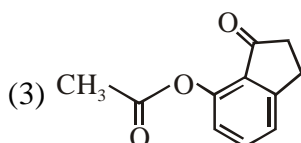
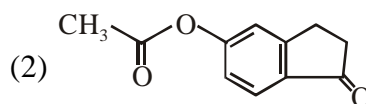
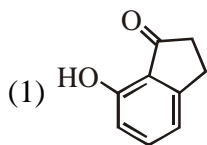
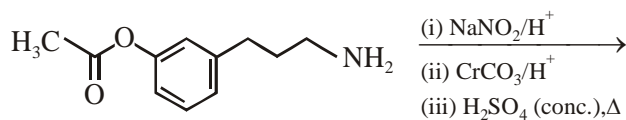
[JEE Main (Jan)-2019]



- (1) (B) < (A) < (D) < (C) (2) (B) < (A) < (C) < (D)  
 (3) (A) < (C) < (D) < (B) (4) (A) < (B) < (C) < (D)

25. The major product of the following reaction is:

[JEE Main (Jan)-2019]



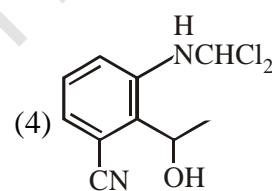
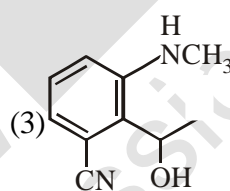
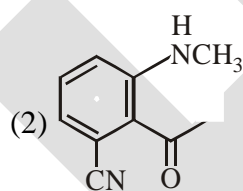
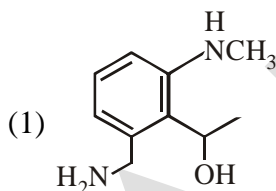
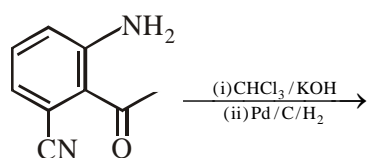
26. Which of the following amines can be prepared by Gabriel phthalimide reaction ?

[JEE Main (Apr)-2019]

- (1) Neo-pentylamine (2) n-butylamine (3) triethylamine (4) t-butylamine

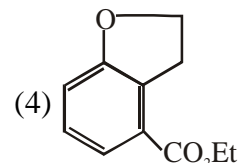
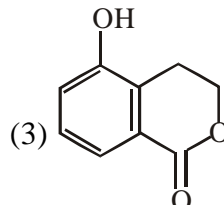
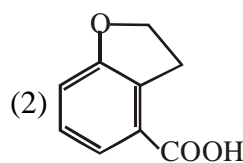
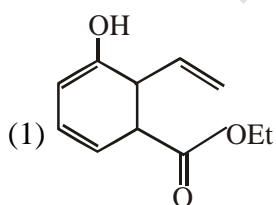
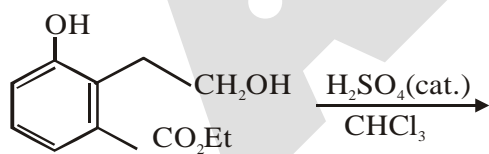
27. The major product obtained in the following reaction is :

[JEE Main (Apr)-2019]



28. The major product of the following reaction is:

[JEE Main (Apr)-2019]



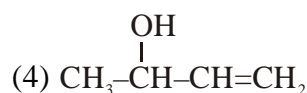
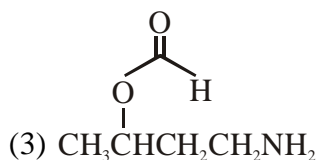
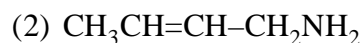
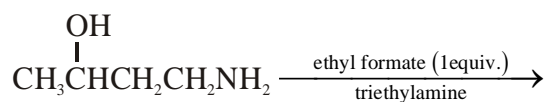
29. Hinsberg's reagent is :

[JEE Main (Apr)-2019]

- (1)  $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$  (2)  $\text{C}_6\text{H}_5\text{COCl}$  (3)  $\text{SOCl}_2$  (4)  $(\text{COCl})_2$

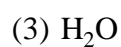
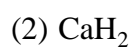
30. The major product of the following reaction is :

[JEE Main (Apr)-2019]



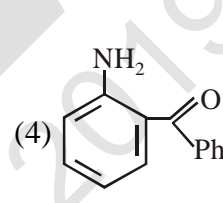
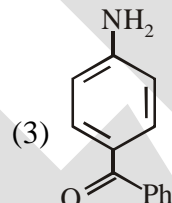
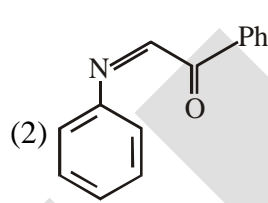
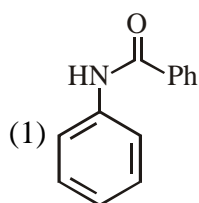
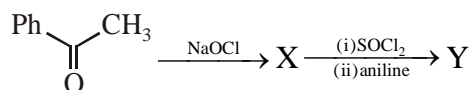
31. Ethylamine ( $\text{C}_2\text{H}_5\text{NH}_2$ ) can be obtained from N-ethylphthalimide on treatment with :

[JEE Main (Apr)-2019]



32. The major product 'Y' in the following reaction is:-

[JEE Main (Apr)-2019]



EXERCISE # IV (B) (JEE ADVANCED)

- Which of the following carboxylic acids undergo decarboxylation easily: [IIT 1995]
 

|                                                                         |                                                                           |
|-------------------------------------------------------------------------|---------------------------------------------------------------------------|
| (A) $\text{C}_6\text{H}_5\text{CO}-\text{CH}_2\text{COOH}$              | (B) $\text{C}_6\text{H}_5\text{COCO}_2\text{H}$                           |
| (C) $\text{C}_6\text{H}_5\underset{\text{OH}}{\text{CH}_2}-\text{COOH}$ | (D) $\text{C}_6\text{H}_5\underset{\text{NH}_2}{\text{CH}_2}-\text{COOH}$ |
- The molecular weight of benzoic acid in benzene as determined by depression in freezing point method corresponds to : [IIT 1996]
 

(A) Ionization of benzoic acid

(B) Dimerisation of benzoic acid

(C) Trimerisation of benzoic acid

(D) Solvation of benzoic acid
- When propionic acid is treated with aqueous  $\text{NaHCO}_3$ ,  $\text{CO}_2$  is liberated. The 'C' of  $\text{CO}_2$  comes from. [IIT 1999]
 

|                     |                           |
|---------------------|---------------------------|
| (A) Methyl group    | (B) Carboxylic acid group |
| (C) methylene group | (D) bicarbonate           |
- Benzoyl chloride is prepared from benzoic acid by: [IIT 2000]
 

|                         |                              |                     |                                       |
|-------------------------|------------------------------|---------------------|---------------------------------------|
| (A) $\text{Cl}_2, h\nu$ | (B) $\text{SO}_2\text{Cl}_2$ | (C) $\text{SOCl}_2$ | (D) $\text{Cl}_2, \text{H}_2\text{O}$ |
|-------------------------|------------------------------|---------------------|---------------------------------------|
- Which of the following acids has the smallest dissociation constant? [IIT 2002]
 

|                                           |                                          |
|-------------------------------------------|------------------------------------------|
| (A) $\text{CH}_3\text{CHF}_2\text{COOH}$  | (B) $\text{FCH}_2\text{CH}_2\text{COOH}$ |
| (C) $\text{BrCH}_2\text{CH}_2\text{COOH}$ | (D) $\text{CH}_3\text{CHBrCOOH}$         |
- When benzamide is treated with  $\text{POCl}_3$ , the product is: [IIT 2004]
 

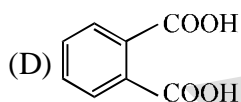
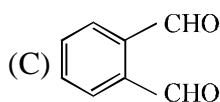
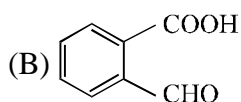
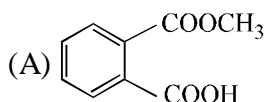
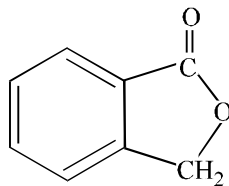
|                  |             |                   |                 |
|------------------|-------------|-------------------|-----------------|
| (A) Benzonitrile | (B) Aniline | (C) Chlorobenzene | (D) Benzylamine |
|------------------|-------------|-------------------|-----------------|
- $$\text{MeO}-\text{C}_6\text{H}_4-\text{CHO} + (\text{X}) \xrightarrow[\text{H}_3\text{O}^+]{\text{CH}_3\text{COONa}} \text{MeO}-\text{C}_6\text{H}_4-\text{CH}=\text{CH}-\text{COCH}_3$$

The compound (X) is [IIT 2005]

|                                        |                                 |
|----------------------------------------|---------------------------------|
| (A) $(\text{CH}_3\text{CO})_2\text{O}$ | (B) $\text{BrCH}_2-\text{COOH}$ |
| (C) $\text{CH}_3\text{COOH}$           | (D) $\text{CHO}-\text{COOH}$    |



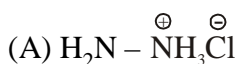
8. Which of the following reactants on reaction with conc. NaOH followed by acidification gives the following lactone as the only product? [IIT 2006]



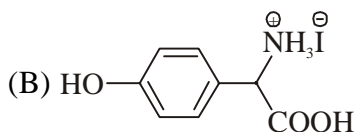
9. Match the compounds in **Column I** with their characteristic test(s)/reaction(s) given in **Column II**. Indicate your answer by darkening the appropriate bubbles of the  $4 \times 4$  matrix given in the ORS. **Column-I**

**Column-II**

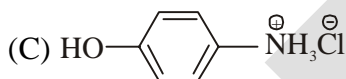
[IIT 2008]



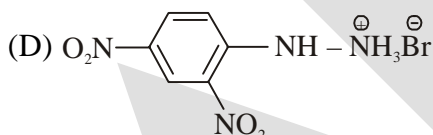
(P) Sodium fusion extract of the compound gives Prussian blue colour with  $\text{FeSO}_4$



(Q) Gives positive  $\text{FeCl}_3$  test



(R) Gives white precipitate with  $\text{AgNO}_3$



(S) Reacts with aldehydes to form the corresponding hydrazone derivative

10. Match each of the compound in Column I with its characteristic reaction(s) in Column II.

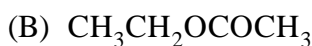
**Column-I**

**Column-II**

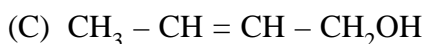
[IIT 2009]



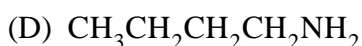
(P) Reduction with  $\text{Pd-C} / \text{H}_2$



(Q) Reduction with  $\text{SnCl}_2 / \text{HCl}$



(R) Development of foul smell on treatment with chloroform and alcoholic KOH

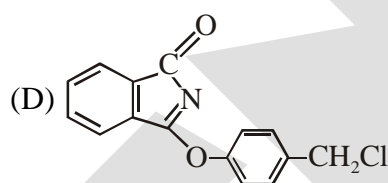
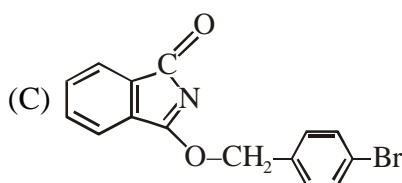
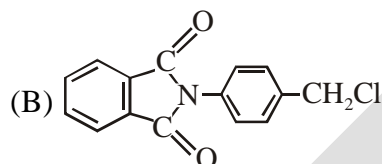
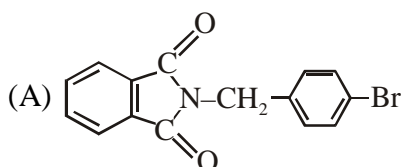
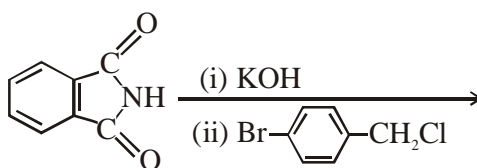


(S) Reduction with diisobutylaluminium hydride (DIBAL-H)

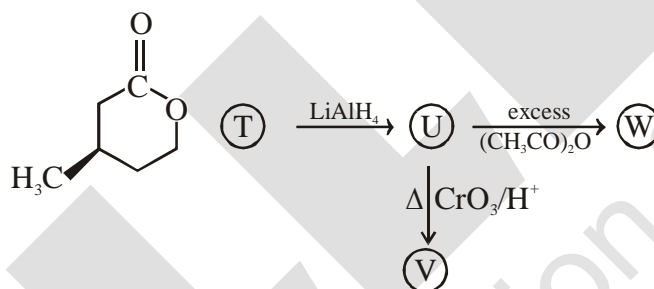
(T) Alkaline hydrolysis

11. The major product of the following reaction is

[IIT 2011]



12. With reference the scheme given, which of the given statement(s) about T, U, V & W is/are correct [IIT 2012]



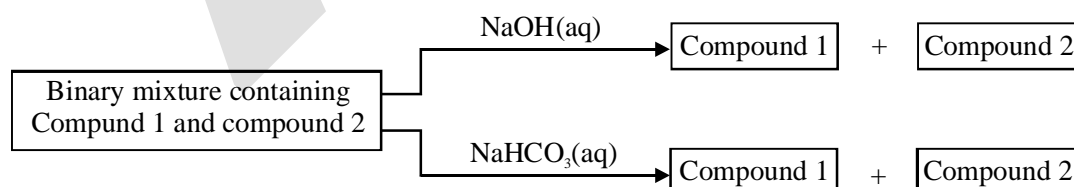
(A) 'T' is soluble in hot aq NaOH

(B) 'U' is optically active

(C) mol formula of W is  $C_{10}H_{18}O_4$

(D) V gives effervescence with aq  $NaHCO_3$

13. Identify the binary mixtures (s) that can be separated into the individual compounds, by differential extraction, as shown in the given scheme - [IIT 2012]



(A)  $C_6H_5OH$  and  $C_6H_5COOH$

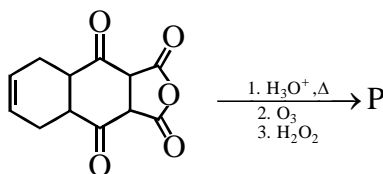
(B)  $C_6H_5COOH$  and  $C_6H_5CH_2OH$

(C)  $C_6H_5CH_2OH$  and  $C_6H_5OH$

(D)  $C_6H_5CH_2OH$  and  $C_6H_5CH_2COOH$

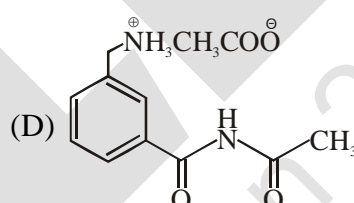
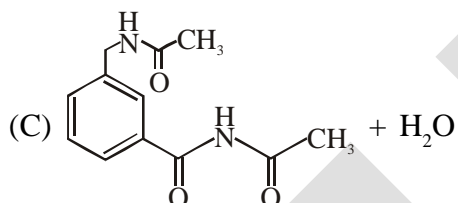
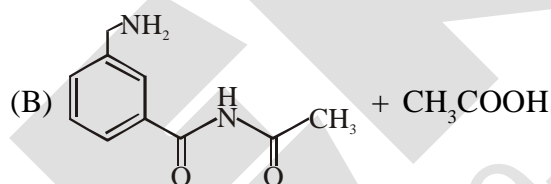
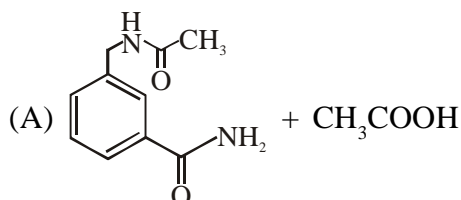
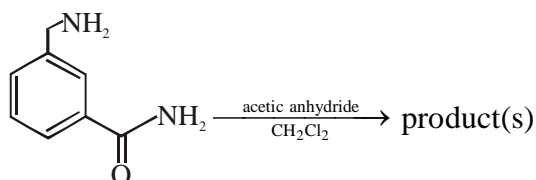
14. The total number of carboxylic acid groups in the product P is

[IIT 2013]



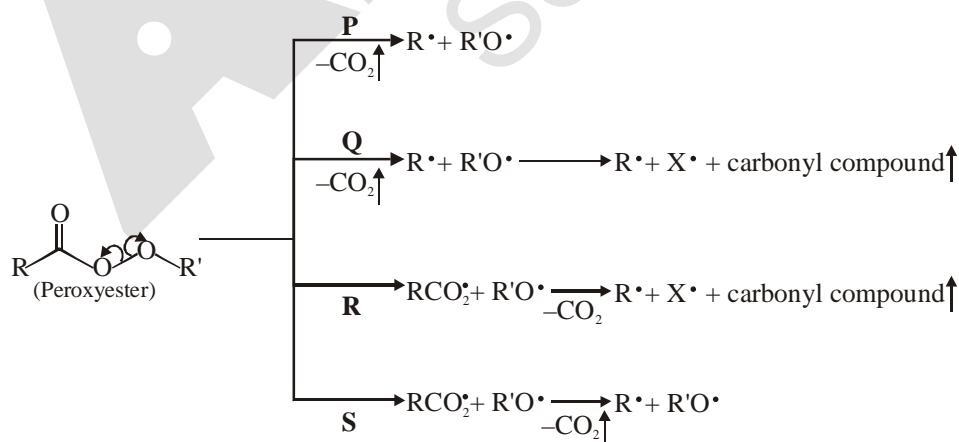
15. In the reaction shown below, the major product(s) formed is / are :

[IIT 2014]



16. Different possible **thermal** decomposition pathways for peroxyesters are shown below. Match each pathway from List-I with an appropriate structure from List-II and select the correct answer using the code given below the lists.

[IIT 2014]



List-I

(P) Pathway P

(Q) Pathway Q

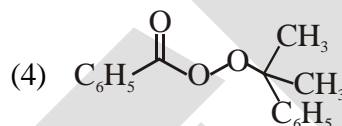
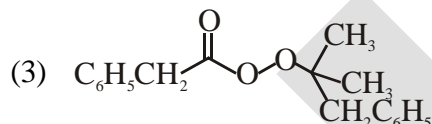
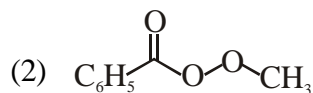
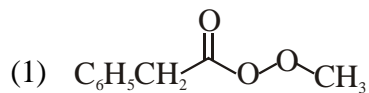
(R) Pathway R

(S) Pathway S

Code :

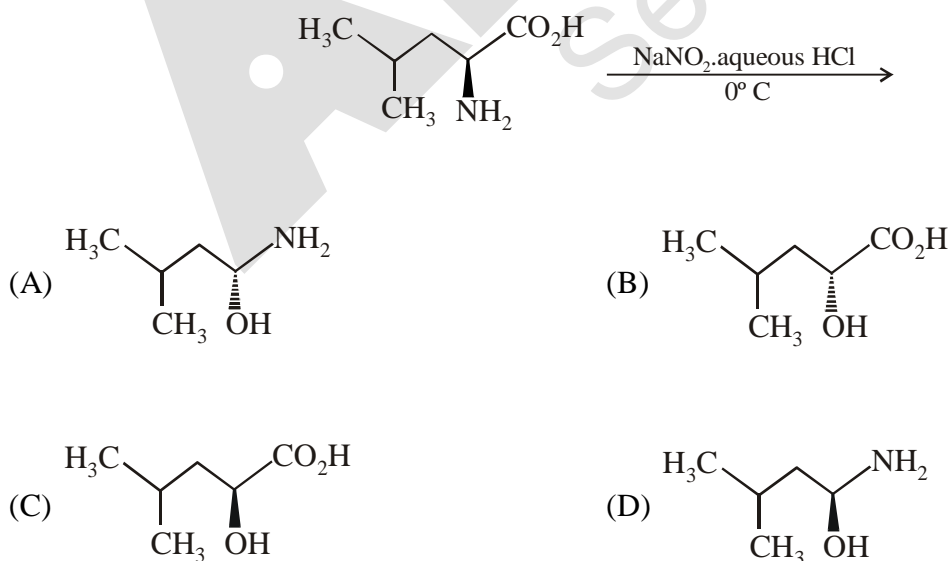
| P     | Q | R | S |
|-------|---|---|---|
| (A) 1 | 3 | 4 | 2 |
| (B) 2 | 4 | 3 | 1 |
| (C) 4 | 1 | 2 | 3 |
| (D) 3 | 2 | 1 | 4 |

List-II



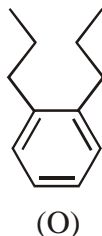
17. The major product of the reaction is :

[IIT 2015]

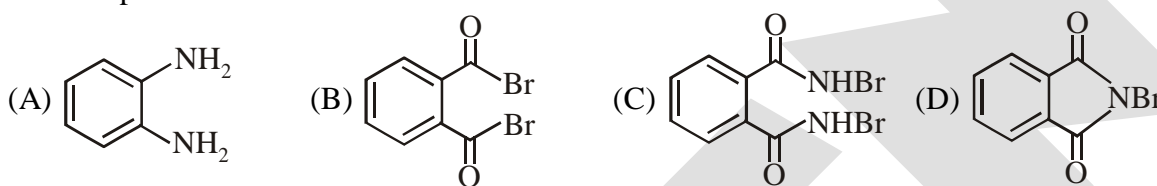


## PARAGRAPH FOR NO. 18 &amp; 19

Treatment of compound **O** with  $\text{KMnO}_4/\text{H}^+$  gave **P**, which on heating with ammonia gave **Q**. The compound **Q** on treatment with  $\text{Br}_2/\text{NaOH}$  produced **R**. On strong heating, **Q** gave **S**, which on further treatment with ethyl 2-bromopropionate in the presence of  $\text{KOH}$  followed by acidification, gave a compound **T**. [IIT-JEE-2016]



18. The compound **R** is :

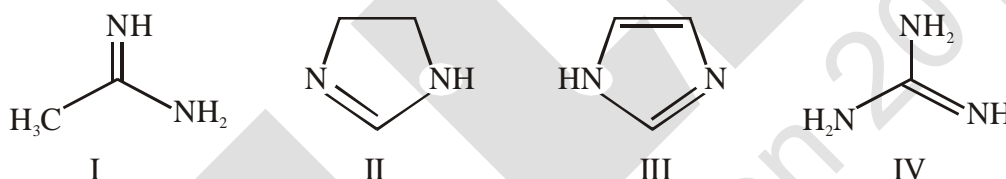


19. The compound **T** is :

- (A) Glycine (B) Alanine (C) Valine (D) Serine

20. The order of basicity among the following compounds is

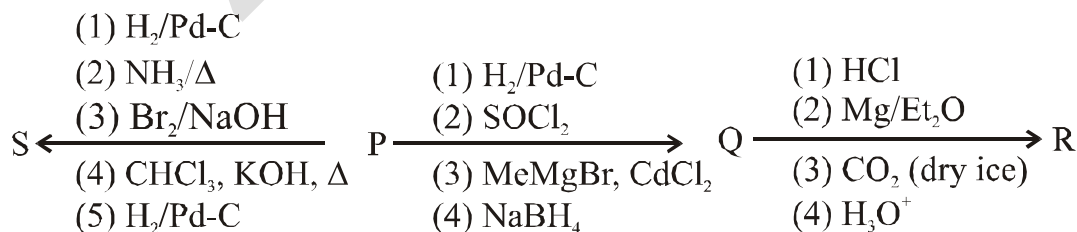
[IIT-JEE(Adv.)-2017]



- (A) II > I > IV > III (B) IV > II > III > I  
(C) I > IV > III > II (D) IV > I > II > III

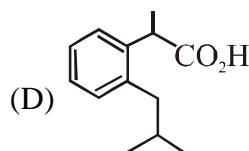
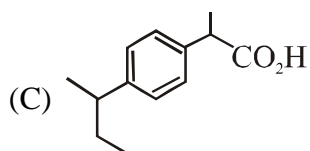
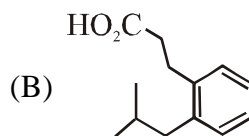
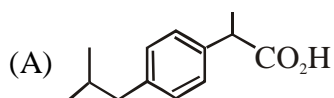
## PARAGRAPH FOR NO. 21 &amp; 22

An organic acid **P** ( $\text{C}_{11}\text{H}_{12}\text{O}_2$ ) can easily be oxidized to a dibasic acid which reacts with ethyleneglycol to produce a polymer dacron. Upon ozonolysis, **P** gives an aliphatic ketone as one of the products. **P** undergoes the following reaction sequences to furnish **R** via **Q**. The compound **P** also undergoes another set of reactions to produce **S**. [IIT-JEE(Adv.)-2018]

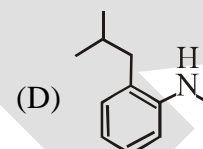
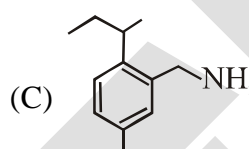
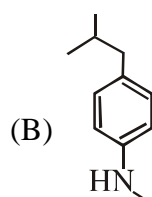
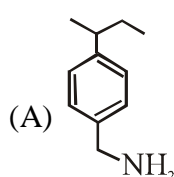


(There are two questions based on PARAGRAPH "A", the question given below is one of them)

21. The compound **R** is



22. The compound **S** is



## ANSWER-KEY

## EXERCISE # I

- |              |              |              |              |
|--------------|--------------|--------------|--------------|
| 1. Ans. (A)  | 2. Ans. (B)  | 3. Ans. (B)  | 4. Ans. (C)  |
| 5. Ans. (C)  | 6. Ans. (A)  | 7. Ans. (B)  | 8. Ans. (C)  |
| 9. Ans. (A)  | 10. Ans. (C) | 11. Ans. (D) | 12. Ans. (B) |
| 13. Ans. (B) | 14. Ans. (B) | 15. Ans. (A) | 16. Ans. (A) |
| 17. Ans. (B) | 18. Ans. (C) | 19. Ans. (B) | 20. Ans. (C) |
| 21. Ans. (B) | 22. Ans. (B) | 23. Ans. (A) | 24. Ans. (B) |
| 25. Ans. (C) |              |              |              |

## EXERCISE # II

- |                  |                  |                    |                |
|------------------|------------------|--------------------|----------------|
| 1. Ans. (A,C,D)  | 2. Ans. (A,C)    | 3. Ans. (A,C,D)    | 4. Ans. (A,B)  |
| 5. Ans. (A,C,D)  | 6. Ans. (A,B,C)  | 7. Ans. (B,C)      | 8. Ans. (C)    |
| 9. Ans. (A,B,D)  | 10. Ans. (A)     | 11. Ans. (A,C)     | 12. Ans. (B,C) |
| 13. Ans. (B)     | 14. Ans. (A,B,C) | 15. Ans. (A,B,C,D) | 16. Ans. (A,D) |
| 17. Ans. (A,B,C) | 18. Ans. (B)     | 19. Ans. (A,B,D)   | 20. Ans. (C,D) |
| 21. Ans. (B,C,D) |                  |                    |                |

## EXERCISE # III

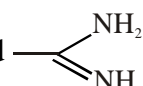
- |                                                |                                          |
|------------------------------------------------|------------------------------------------|
| 1. Ans. (A)→P, S ; (B)→Q, S ; (C)→P, S ; (D)→R |                                          |
| 2. Ans. (A)→S ; (B)→R ; (C)→P ; (D)→Q          | 3. Ans. (A)→S ; (B)→R ; (C)→P ; (D)→Q    |
| 4. Ans. (A)→R ; (B)→S ; (C)→Q ; (D)→P          | 5. Ans. (A)→P ; (B)→Q ; (C)→S ; (D)→R, S |
| 6. Ans. (A)→P ; (B)→R ; (C)→P, S ; (D)→Q       |                                          |
| 7. Ans. (4)                                    | 8. Ans. (4)                              |
| 9. Ans. (5)                                    | 10. Ans. (9)                             |

## EXERCISE # IV (A) (JEE-MAIN)



- |              |              |              |              |
|--------------|--------------|--------------|--------------|
| 1. Ans. (2)  | 2. Ans. (1)  | 3. Ans. (4)  | 4. Ans. (4)  |
| 5. Ans. (4)  | 6. Ans. (2)  | 7. Ans. (4)  | 8. Ans. (4)  |
| 9. Ans. (2)  | 10. Ans. (1) | 11. Ans. (2) | 12. Ans. (1) |
| 13. Ans. (1) |              |              |              |
| 14. Ans. (2) |              |              |              |

**Sol.** Order of base nature depends on electron donation tendency.

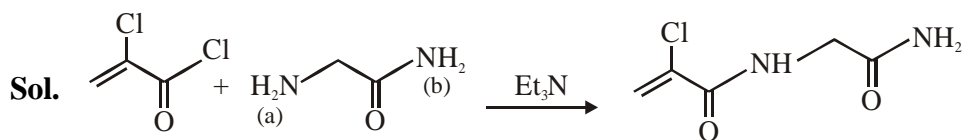
In compound  nitrogen is  $sp^2$  hybridized so least basic among all given compound.

compound  is very strong nitrogenous organic base as lone pair of one nitrogen delocalize in resonance and make another nitrogen negatively charged and conjugate acid have two equivalent resonating structure.

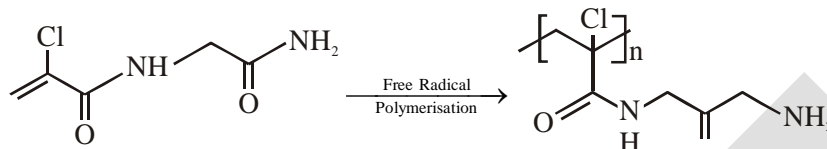
Thus it is most basic in given compounds.

  $\text{NHCH}_3$  (secondary amine) more basic than   $\text{NH}_2$  (primary amine)

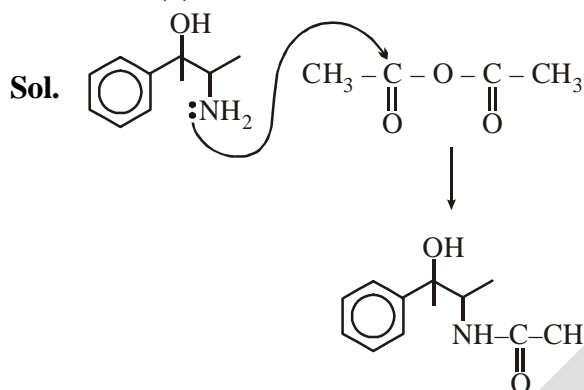
15. Ans. (4)



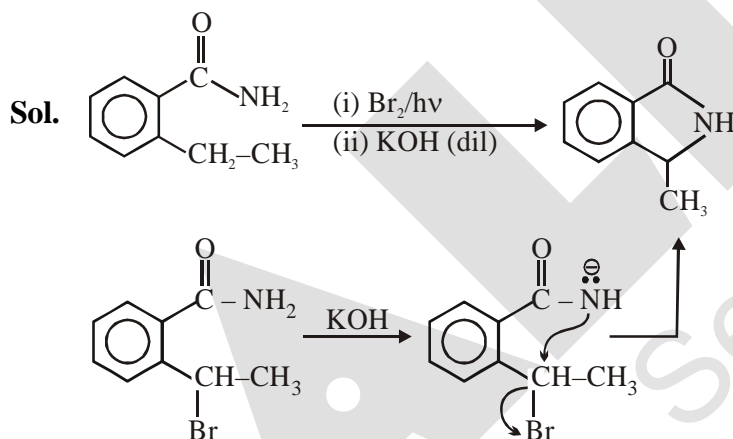
NH<sub>2</sub>(a) will act as nucleophile as (b) is having delocalised lonepair.



16. Ans. (3)



17. Ans. (3)



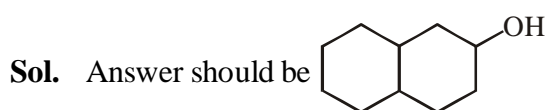
18. Ans. (4)

Sol. Adipic acid  $\text{CO}_2\text{H}-(\text{CH}_2)_4-\text{CO}_2\text{H} \xrightarrow[\text{agent}]{\text{dehydrating}}$  7 membered cyclic anhydride (Very unstable)

19. Ans. (2)

Sol. More is the electrophilic character of carbonyl group of ester faster is the alkaline hydrolysis.

20. Ans. (Bonus)

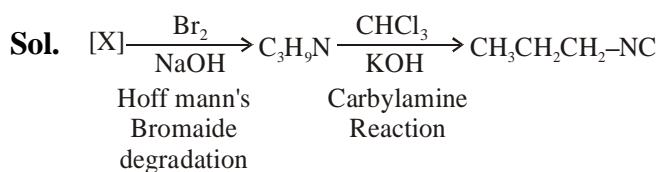


21. Ans. (2)

22. Ans. (3)



23. Ans. (3)

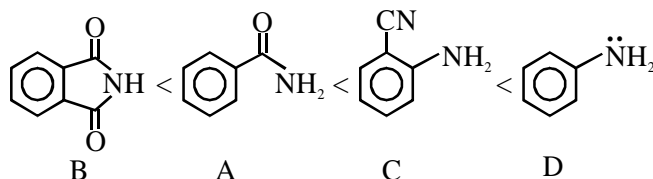


Thus [X] must be an aride with one carbon more than is amine.

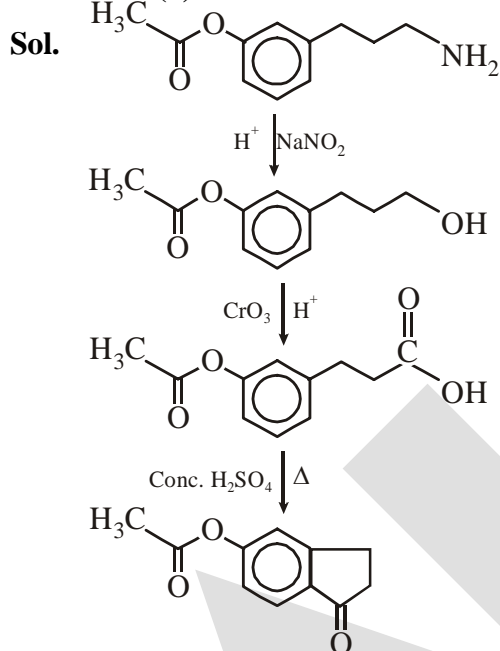
Thus [X] is  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CONH}_2$

24. Ans. (2)

Sol. Nucleophilicity order

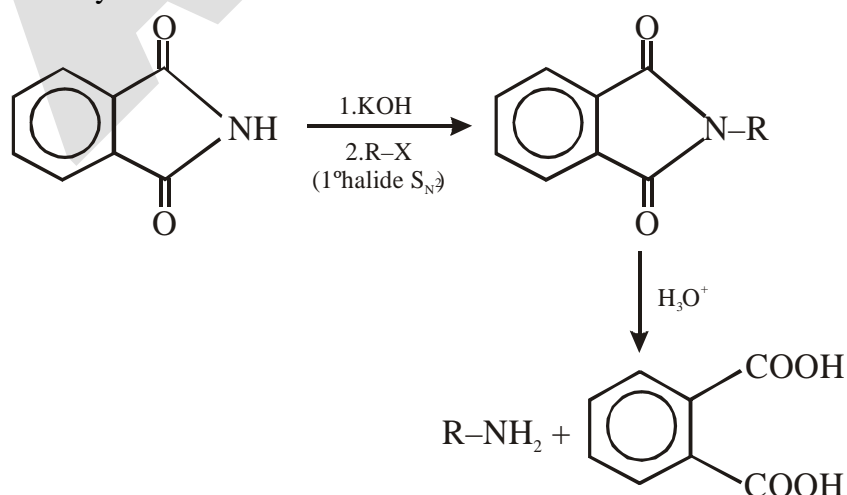


25. Ans. (4)

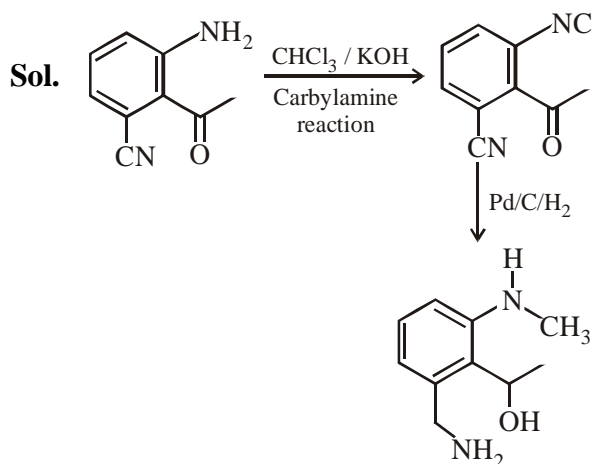


26. Ans. (2)

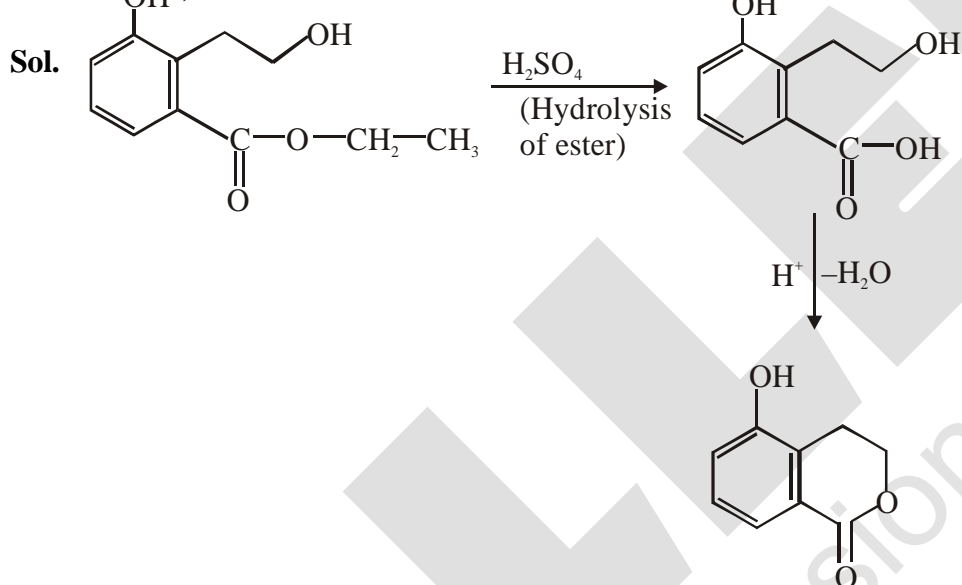
Sol. Gabriel phthalimide synthesis :



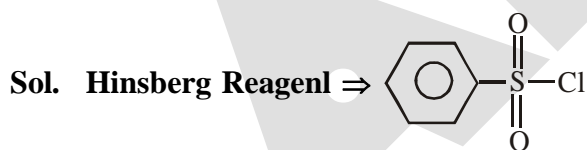
27. Ans. (1)



28. Ans. (3)

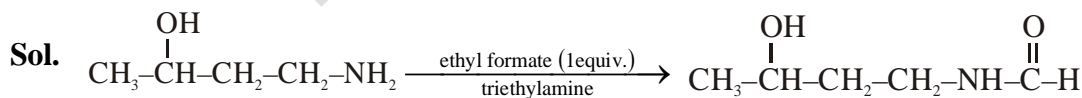


29. Ans. (1)



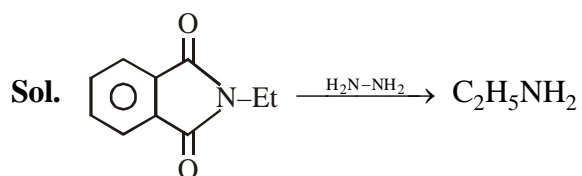
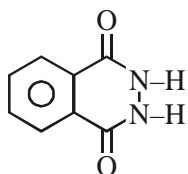
[Benzene Sulphonyl chloride]

30. Ans. (1)

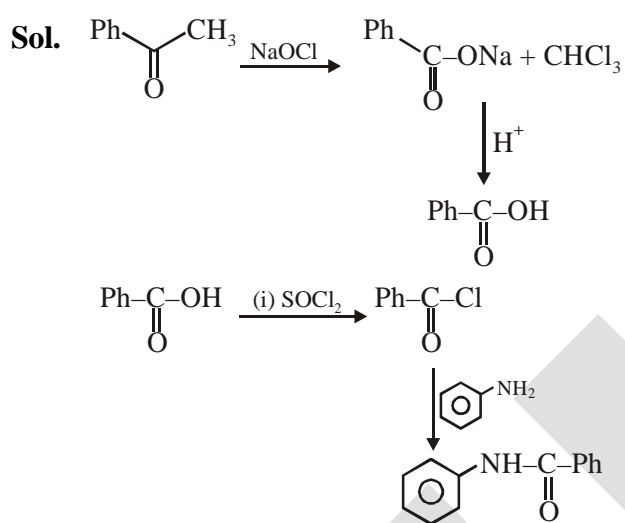


as  $\text{NH}_2$  is a better nucleophile than  $\text{OH}$ .

31. Ans. (4)

reagent is  $\text{NH}_2\text{-NH}_2$  byproduct will be

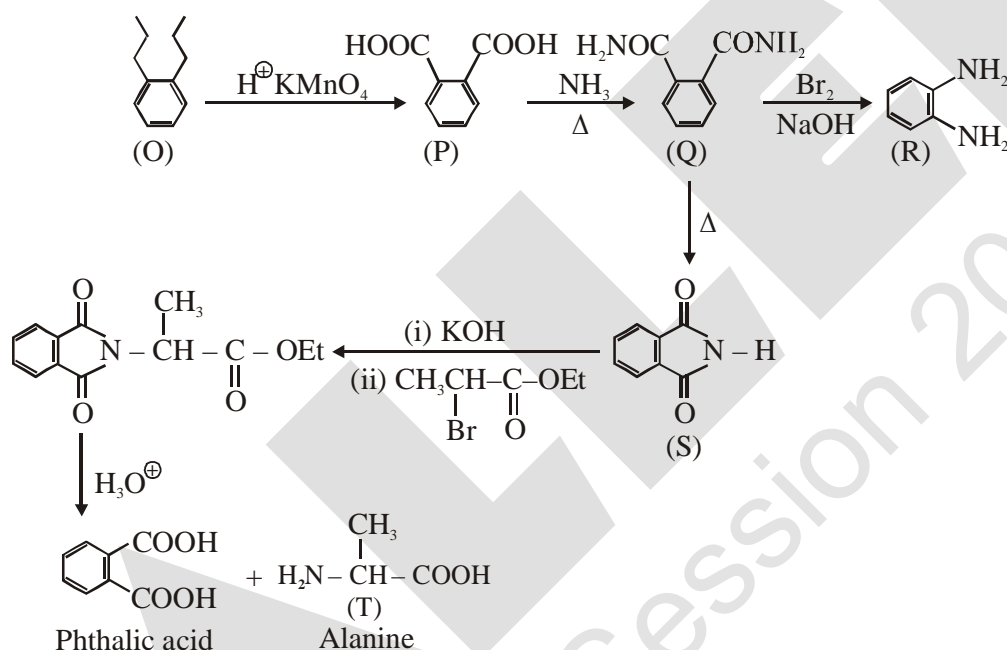
32. Ans. (1)



EXERCISE # IV (B) (JEE ADVANCED)

1. Ans. (A)      2. Ans. (B)      3. Ans. (D)
4. Ans. (C)      5. Ans. (C)      6. Ans. (A)      7. Ans. (A)
8. Ans. (C)      9. Ans. (A)→R, S ; (B)→P, Q ; (C)→P, Q, R ; (D)→P, S
10. Ans. (A)→P, Q, S, T ; (B)→P, S, T ; (C)→P ; (D)→R      11. Ans. (A)
12. Ans. (A, C, D)      13. Ans. (B, D)      14. Ans. (2)      15. Ans. (A)
16. Ans. (A)      17. Ans. (C)
18. Ans. (A)
19. Ans. (B)

Solution 18 & 19.



Q to R is Hoffmann's bromamide degradation reaction

S to T is Gabriel's phthalimide synthesis

20. Ans. (D)  $\text{IV} > \text{I} > \text{II} > \text{III}$

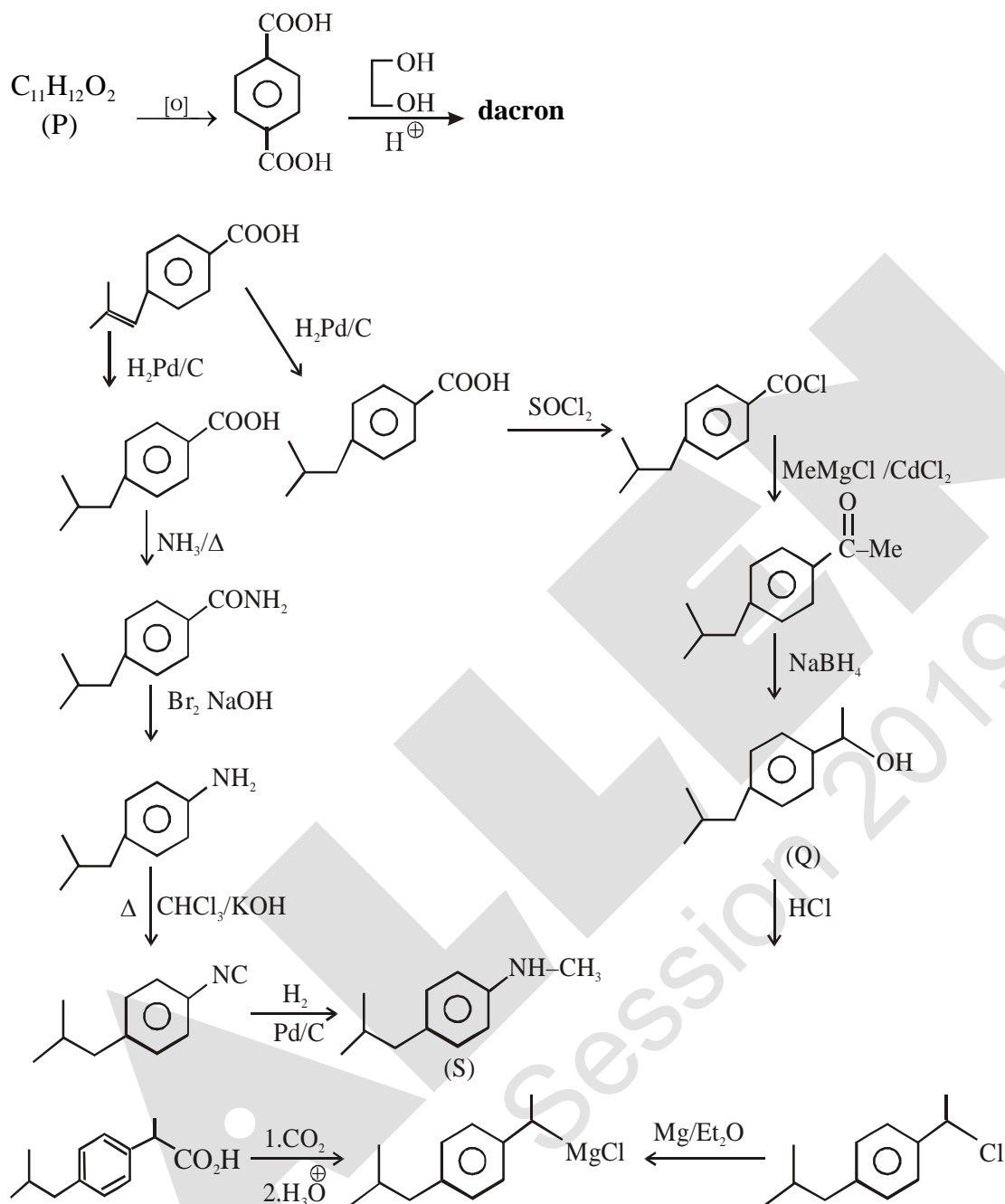
Sol. Basic strength  $\propto$  stability of conjugated acid.

$$\propto +\text{M} / +\text{H} / +\text{I}$$

21. Ans. (A)

22. Ans. (B)

## Solution 21 &amp; 22.



## Important Notes

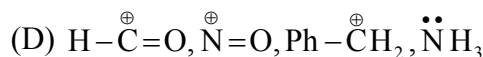
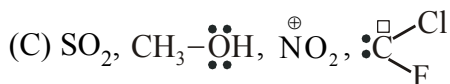
## **HALOGEN DERIVATIVES**

ALLEN  
Session 2019-20

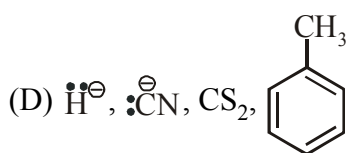
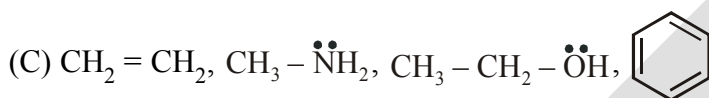
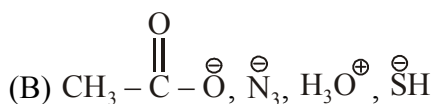
# HALOGEN DERIVATIVES

## EXERCISE # I (MAINS ORIENTED)

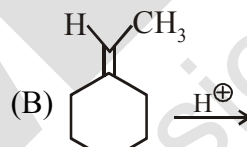
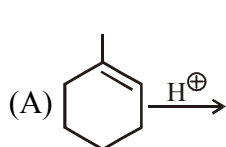
1. Identify set of electrophiles :



2. Identify set of nucleophiles :



3. Which of the following will form 2° carbocation?



4. Incorrect statement about carbocation is :

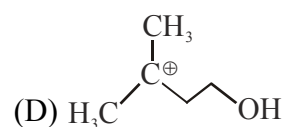
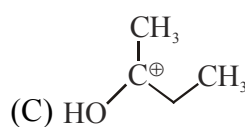
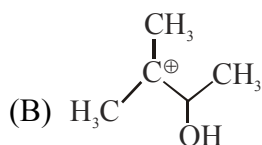
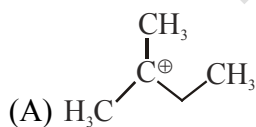
(A) It is lewis acid

(B) It has 6 electrons in valency shell

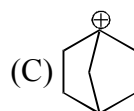
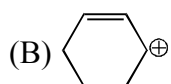
(C) It is electrophile

(D) It is always trigonal planer

5. Which of the following carbocation is most stable ?



6. Which carbocation is least likely to be formed as an intermediate ?

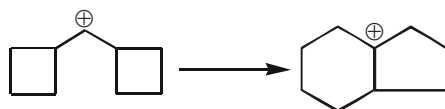




7. Which one of the following carbocation would you expect to rearrange :

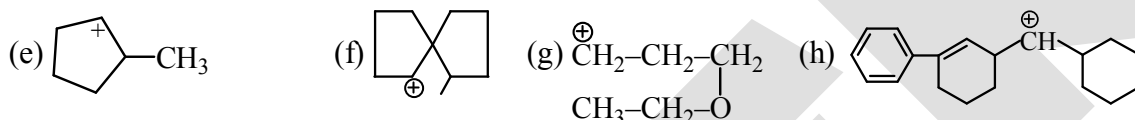


8. How many 1,2-shifts are involved during the course of following reaction :



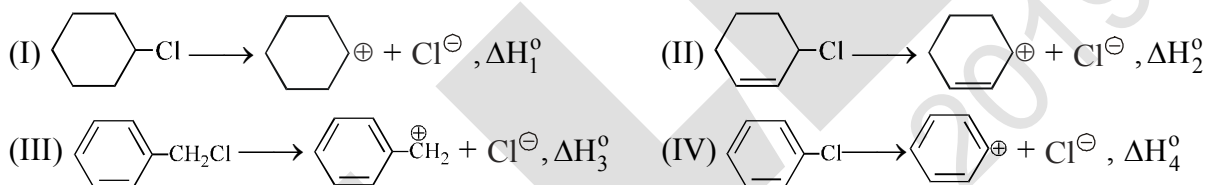
(A) 1 (B) 2 (C) 3 (D) 4

9. How many following carbocation undergo re-arrangement -



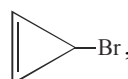
(A) 5 (B) 8 (C) 6 (D) 7

10. For the reactions

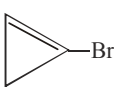


The correct decreasing order of enthalpies of reaction for producing carbocation is :

(A)  $\Delta H_1^0 > \Delta H_2^0 > \Delta H_3^0 > \Delta H_4^0$  (B)  $\Delta H_4^0 > \Delta H_1^0 > \Delta H_2^0 > \Delta H_3^0$   
 (C)  $\Delta H_3^0 > \Delta H_2^0 > \Delta H_1^0 > \Delta H_4^0$  (D)  $\Delta H_2^0 > \Delta H_1^0 > \Delta H_4^0 > \Delta H_3^0$

11. , which is not the correct statement :

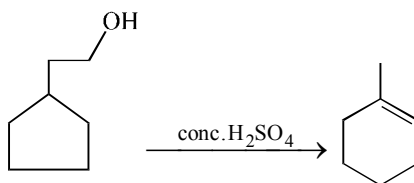
(A) I is more soluble in water than bromocyclopropane  
 (B) I gives pale yellow ppt. on addition with aq.  $\text{AgNO}_3$   
 (C) I is having lower dipole moment than bromocyclopropane

(D) I is more ionic than 

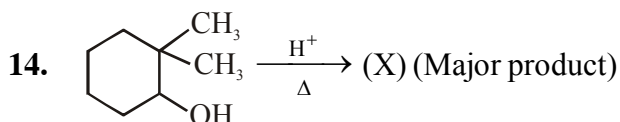
12. A solution of (–) –1-chloro–1-phenylethane in toluene racemises slowly in the presence of a small amount of  $\text{SbCl}_5$ , due to the formation of :-

(A) carbanion (B) Carbene (C) carbocation (D) free radical

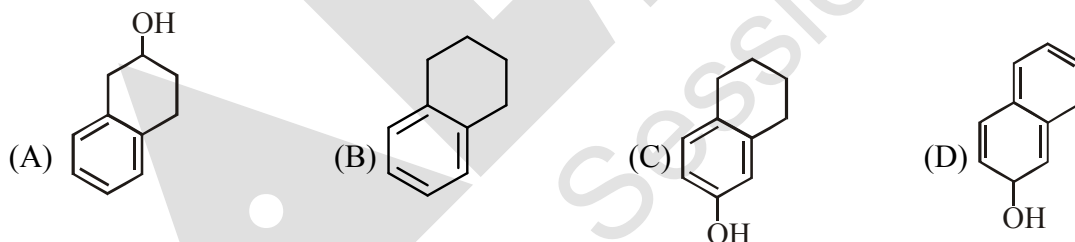
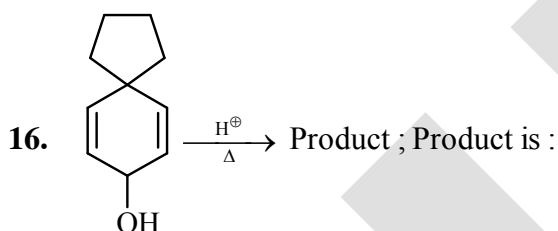
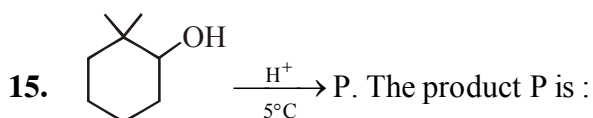
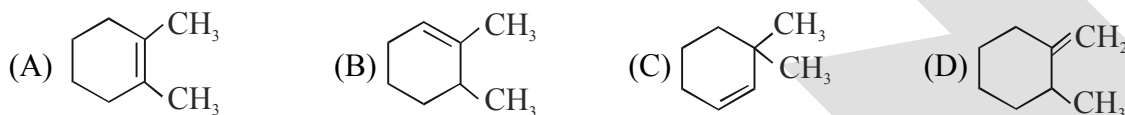
13. How many 1,2-Shifts of carbocation intermediate are involved during the course of following reaction :



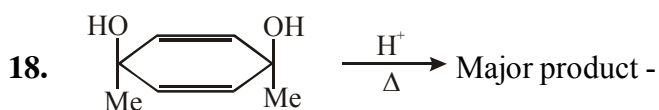
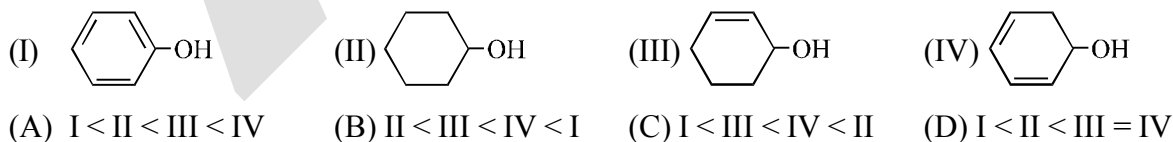
- (A) 1 (B) 2 (C) 3 (D) 4



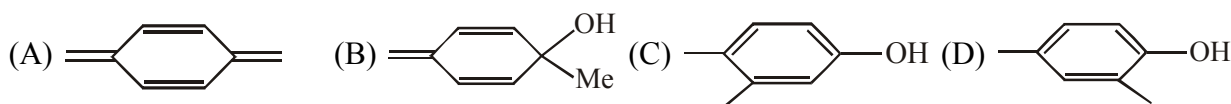
Major product (X) is :



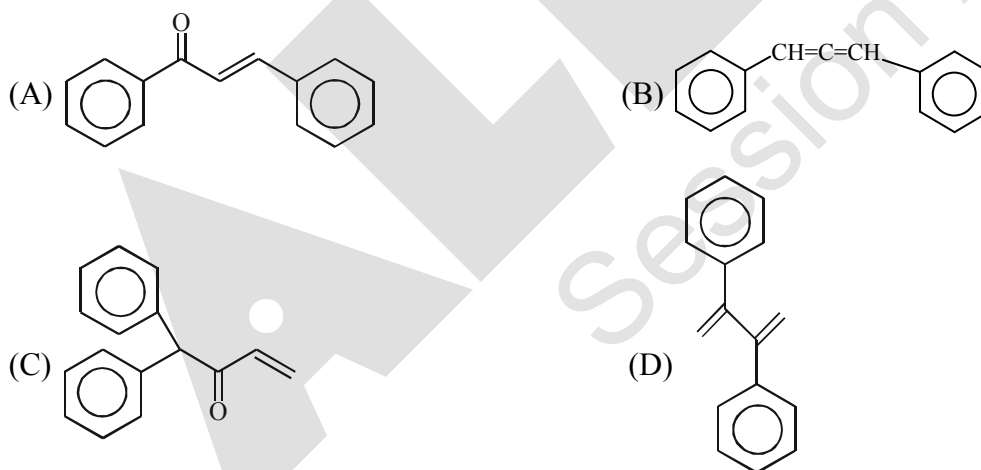
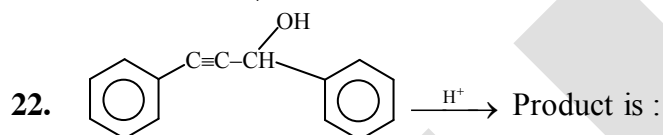
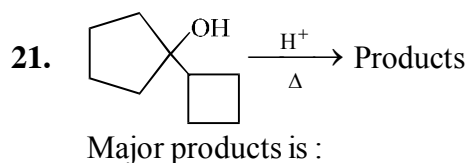
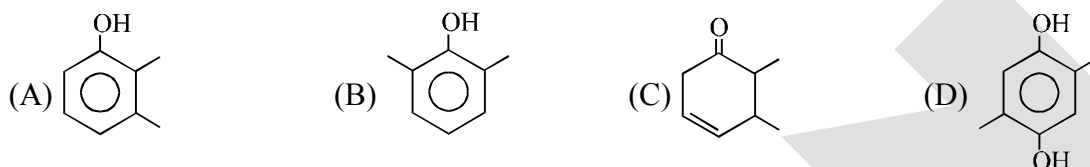
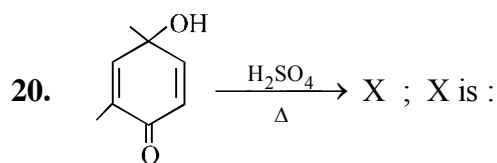
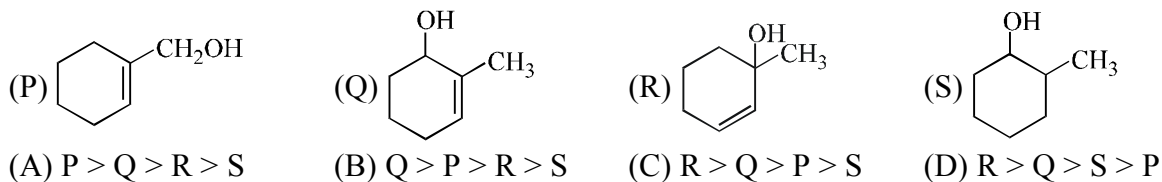
17. Among the given compounds, the correct order of rate of dehydration is :



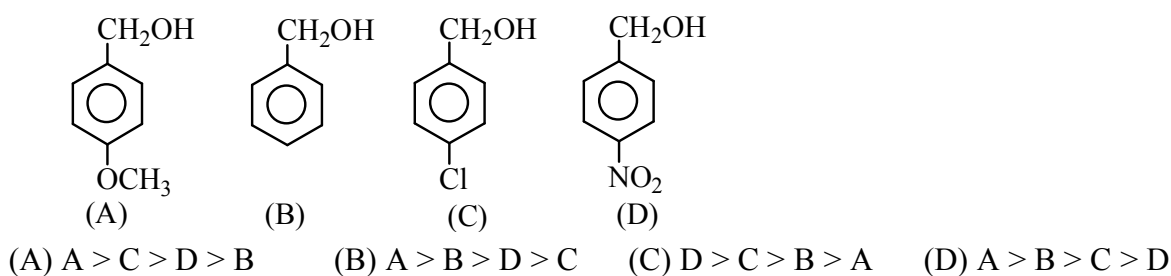
Major product is :



19. Identify the correct order of rate of dehydration when given compounds are treated with conc.  $\text{H}_2\text{SO}_4$  :

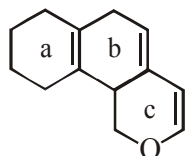


23. What is the decreasing order of rate of reaction with HBr for the following benzyl alcohol and its derivative :



24. Which will dehydrate at fastest rate by  $\text{H}_3\text{PO}_4$  :

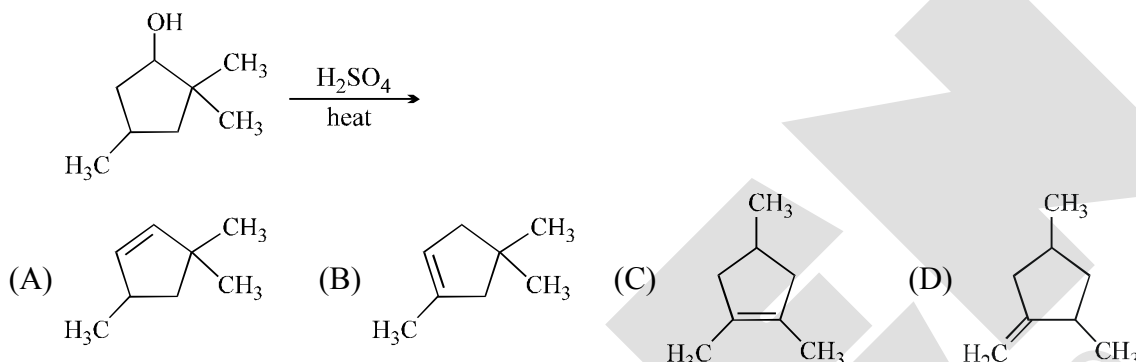
- (A) 2-methyl butan-2-ol (B) 3-methyl butan-2-ol  
(C) Butan-1-ol (D) 2-methyl butan-1-ol



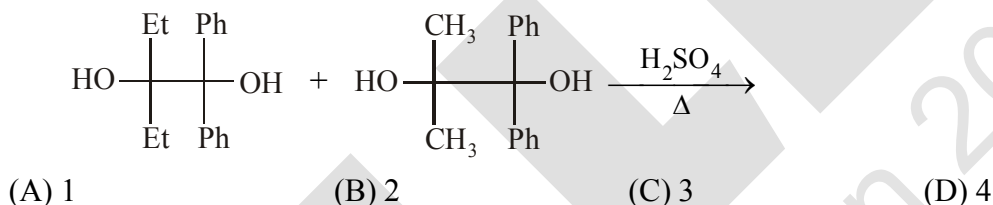
25. The double bond which is most reactive towards attack of electrophile :

- (A) a (B) b (C) c (D) None

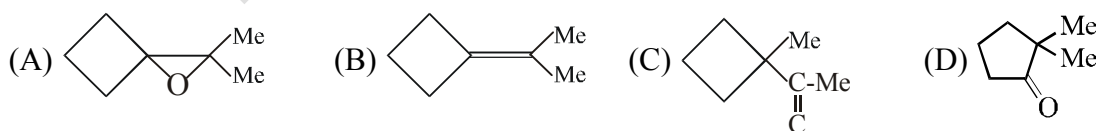
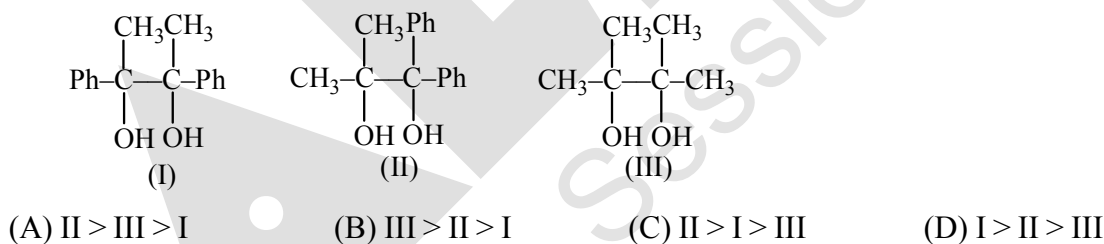
26. The major product formed in the following reaction is :



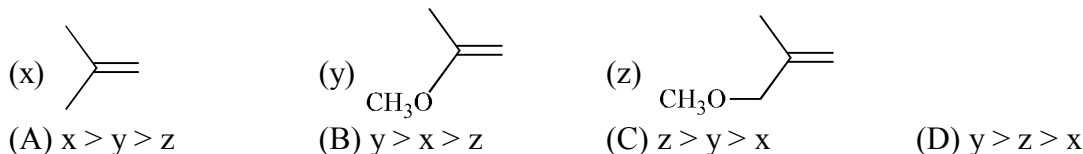
27. How many products are obtained in the given reaction :



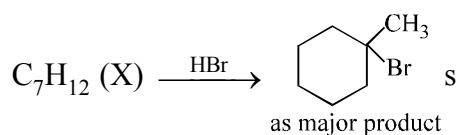
28. Compare rate of reaction towards pinacol pinacolone rearrangement.



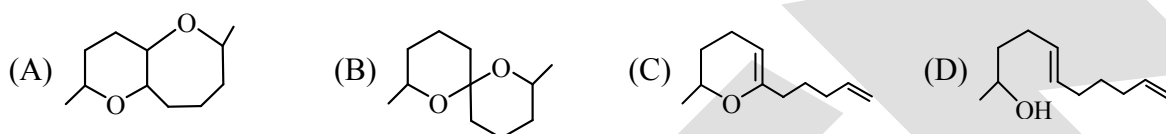
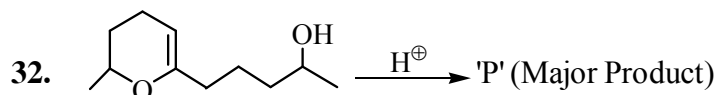
30. What is the order of reactivity with HBr :



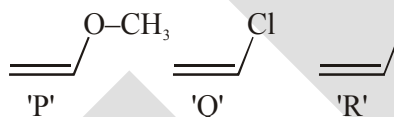
31. In the given reaction



(X) can not be :



33. Arrange the following compounds in decreasing order of electrophilic addition :

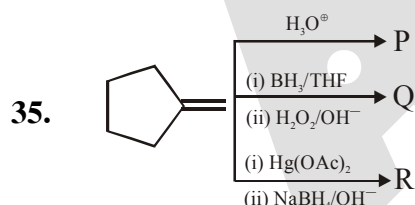


(A)  $P > Q > R$  (B)  $P > R > Q$  (C)  $R > P > Q$  (D)  $R > Q > P$



What is stereochemistry of product :

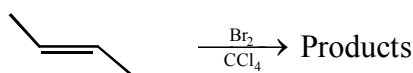
(A) Racemic mixture (B) Optically inactive  
(C) Mixture of diastereomers (D) Meso product



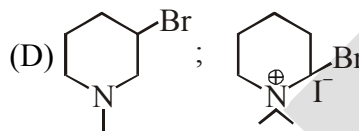
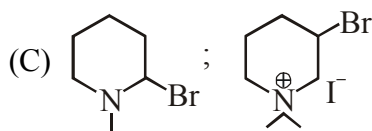
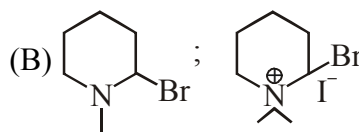
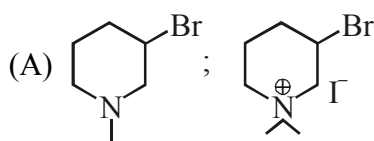
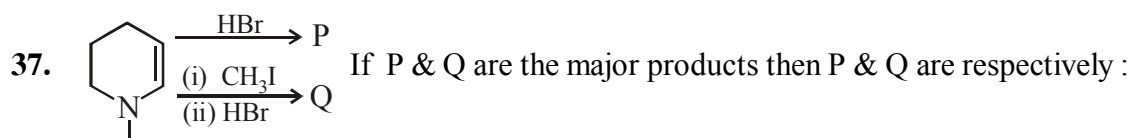
Correct statement regarding products P, Q & R

(A) Product P & R are same (B) Product Q & R are same  
(C) P & Q are functional isomers (D) Product P, Q & R all are different

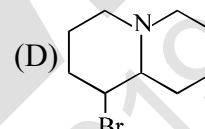
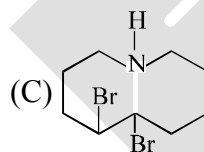
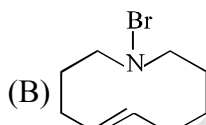
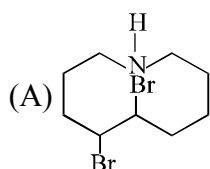
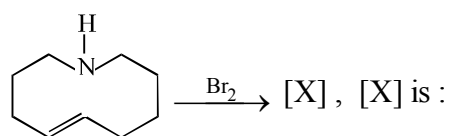
36. Select the incorrect statement about the product mixture in the following reaction :



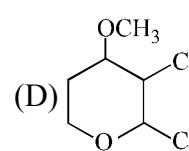
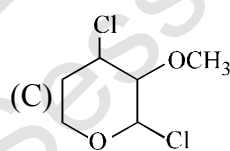
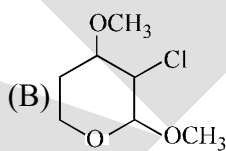
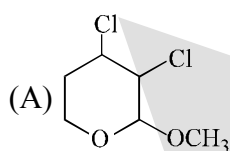
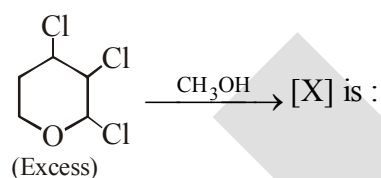
(A) It is optically active (B) It is racemic mixture  
(C) It is a resolvable mixture (D) It is a mixture of erythro compounds



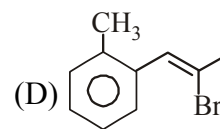
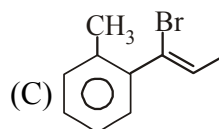
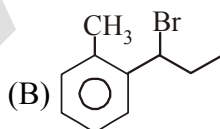
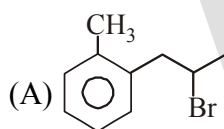
**38.** In the given reaction :



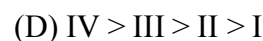
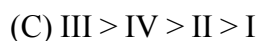
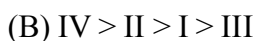
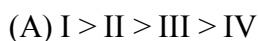
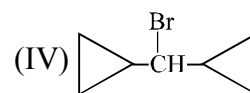
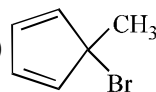
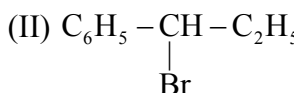
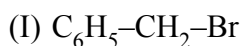
**39.** In the given reaction:



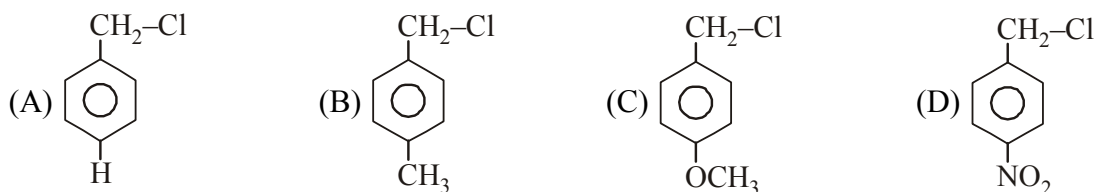
**40.** Which compound undergoes hydrolysis by the  $S_N1$  mechanism at the fastest rate?



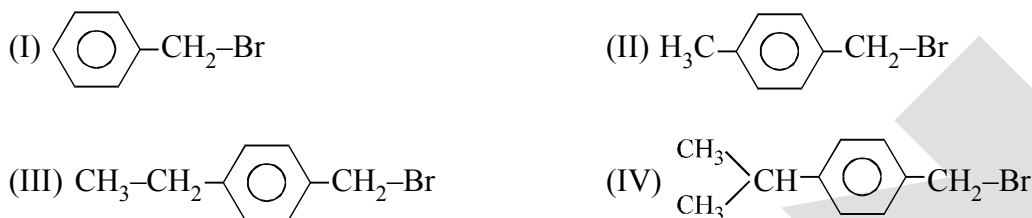
**41.** Arrange the following compounds in decreasing order of their reactivity for hydrolysis reaction



42. Which of the following is most reactive toward  $S_N1$  reaction.

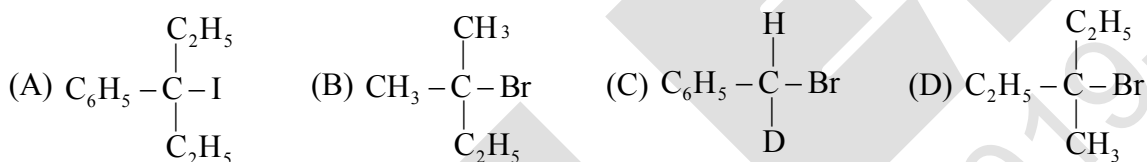


43. Arrange the following compounds in order of decreasing rate of hydrolysis for  $S_N1$  reaction:

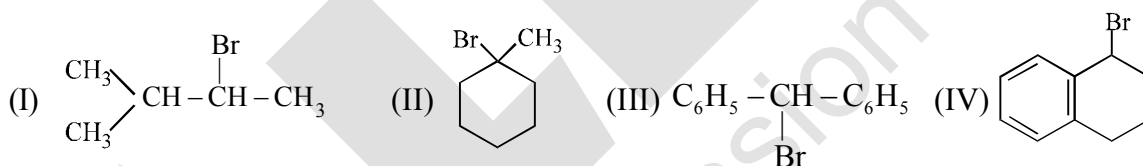


(A) II > III > IV > I (B) IV > III > II > I (C) III > IV > II > I (D) I > II > III > I

44. Which one of the following compounds will give enantiomeric pair on treatment with HOH?



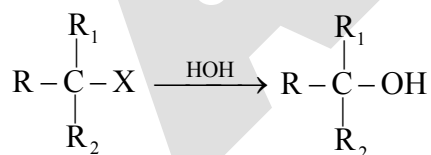
45. Consider the  $S_N1$  solvolysis of the following halides in aqueous formic acid:



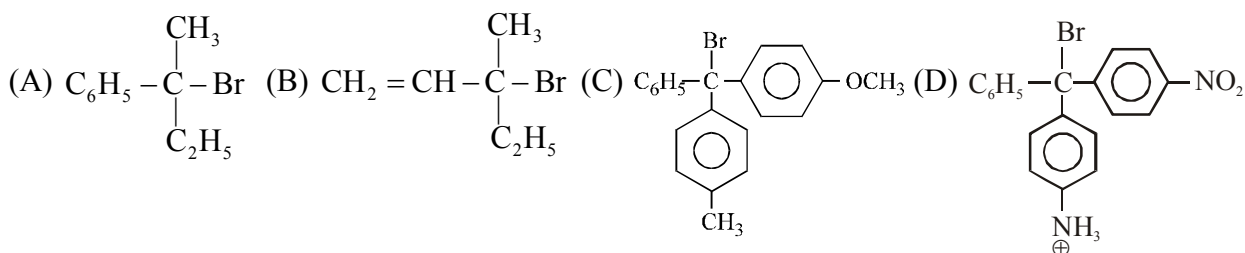
Decide decreasing order of reactivity of above alkyl halide?

(A) III > IV > II > I (B) II > IV > I > III (C) I > II > III > IV (D) III > I > II > IV

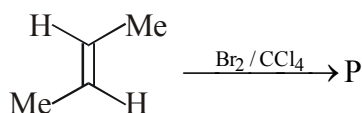
46. For the given reaction



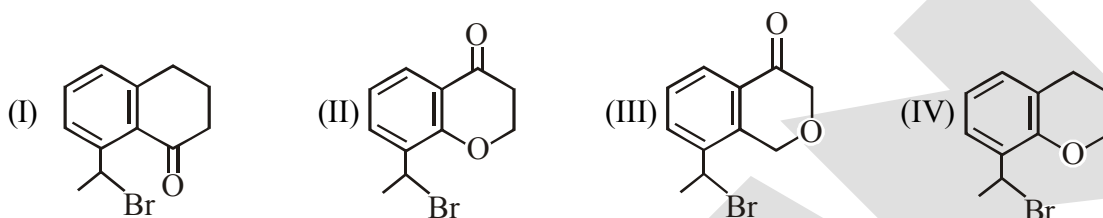
Which substrate will give maximum racemisation?



47. Select incorrect statements about the product (P) of the reaction :

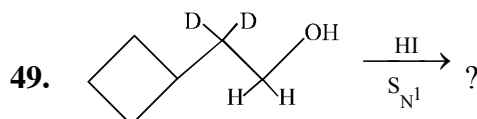


- (A) P is optically inactive due to internal compensation  
 (B) P is optically inactive due to the presence of plane of symmetry in the molecule  
 (C) The structure of P can have three optical isomers possible.  
 (D) P can have four possible optical isomers.
48. Consider the following molecules :



The correct decreasing ease of hydrolysis of alkyl halide is :

- (A) II > III > IV > I (B) II > IV > III > I (C) II > I > III > IV (D) IV > II > III > I

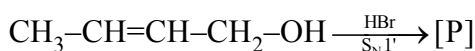


Major product is:



Find out the correct statement about the reaction.

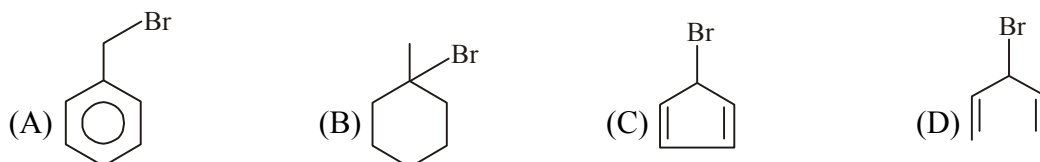
- (A) Among the products 48% S and 48% R configuration containing molecules are present  
 (B) Among the products 50% S and 50% R configuration containing molecules are present  
 (C) Among the products 48% S and 52% R configuration containing molecules are present  
 (D) Among the products 52% S and 48% R configuration containing molecules are present
51. In the given reaction the product [P] can be :



- (A)  $\text{CH}_3\text{--CH=CH--CH}_2\text{--Br}$  (B)  $\text{CH}_3\text{--}\overset{\text{Br}}{\underset{|}{\text{CH}}}\text{--CH=CH}_2$   
 (C)  $\text{CH}_2\text{=CH--CH=CH}_2$  (D)  $\text{CH}_3\text{--}\overset{\text{Br}}{\underset{|}{\text{CH}}}\text{--CH}_2\text{--CH}_2\text{--OH}$



52. Which of the following can not give  $S_N1$  reaction easily?



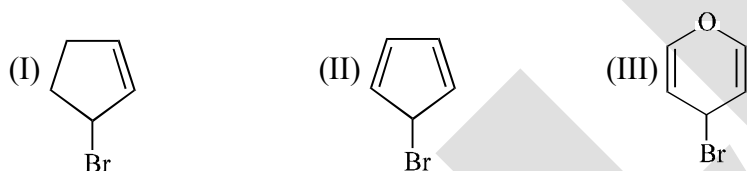
53. Which one of the following compounds will be most reactive for  $S_N1$  reactions?



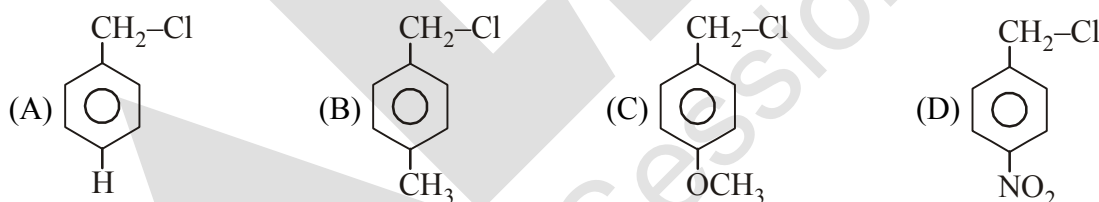
54. Which of the following compounds is most rapidly hydrolysed by  $S_N1$  mechanism?



55. Among the bromides I–III given below, the order of reactivity in  $S_N1$  reaction is:



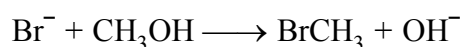
56. Which of the following is most reactive toward  $S_N2$ .



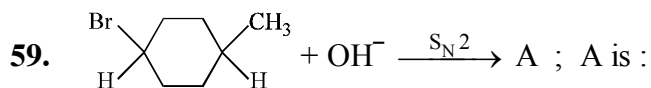
57. For reaction  $CH_3Br + OH^- \longrightarrow CH_3OH + Br^-$  the rate of reaction is given by the expression :

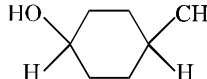
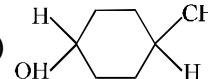


58. Select suitable reason for non-occurrence of the following reaction.



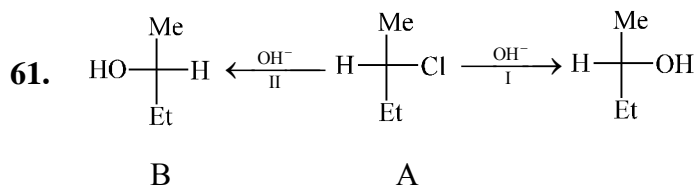
- (A) Attacking nucleophile is stronger one  
(B) Leaving group is a stronger base than nucleophile  
(C) Alcohols are not good substrate for  $S_N$  reaction  
(D) Hydroxide ions are weak bases



- (A)  (B)  (C) Both (D) None

60. The reactivity of 2-bromo-2-methylbutane (I), 1-bromopentane (II) and 2-bromopentane (III) towards S<sub>N</sub>2 displacement is such that :

- (A) I > II > III (B) I > III > II (C) II > III > I (D) II > I > III



Mechanism involved :

- (A) I can't be S<sub>N</sub>1 (B) II can't be S<sub>N</sub>2 (C) I S<sub>N</sub>1 & II S<sub>N</sub>2 (D) I S<sub>N</sub>2 & II S<sub>N</sub>1
62. In which of the following replacement of Cl<sup>-</sup> is most difficult ?

- (A)  (B)  (C)  (D) 

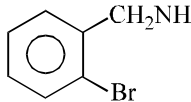
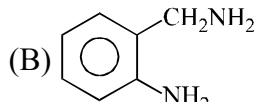
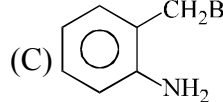
63. Arrange these compounds in order of increasing S<sub>N</sub>2 reaction rate :

- (I)  (II)  (III)  (IV) 

- (A) III < I < II < IV (B) III < II < I < IV (C) IV < III < I < II (D) III < IV < I < II
64. Which reaction proceeds faster with NaI in DMSO ?

- (A)  (B)  (C)  (D) 

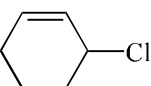
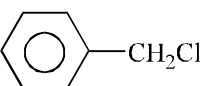


- (A)  (B)  (C)  (D) All of these

66. The given compound CH<sub>3</sub>-O-CH<sub>2</sub>-Br gives which one of the following reactions:

- (A) Only S<sub>N</sub>1 (B) Only S<sub>N</sub>2  
 (C) S<sub>N</sub>1 as well as S<sub>N</sub>2 (D) E<sub>1</sub> only

67. Which will give white ppt. with  $\text{AgNO}_3$ ?

- (A)  (B)  (C)  (D) Both A & C

68. Consider the following groups :

- (I)  $-\text{OAc}$  (II)  $-\text{OMe}$  (III)  $-\text{OSO}_2\text{Me}$  (IV)  $-\text{OSO}_2\text{CF}_3$

The order of leaving group nature is:

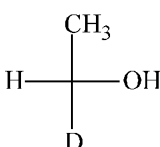
- (A)  $\text{I} > \text{II} > \text{III} > \text{IV}$  (B)  $\text{IV} > \text{III} > \text{I} > \text{II}$  (C)  $\text{III} > \text{II} > \text{I} > \text{IV}$  (D)  $\text{II} > \text{III} > \text{IV} > \text{I}$

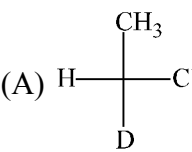
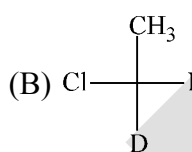
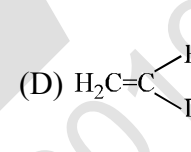
69. When ethyl bromide is treated with moist  $\text{Ag}_2\text{O}$ , the main product is:

- (A) Ethyl ether (B) Ethanol (C) Ethoxy ethane (D) All of these

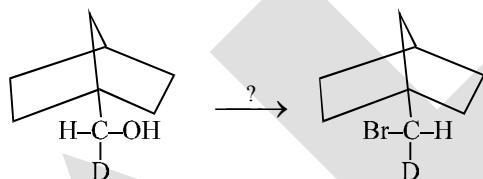
70. When ethyl bromide is treated with dry  $\text{Ag}_2\text{O}$ , the main product is:

- (A) Ethyl ether (B) Ethanol (C) Ethoxy ethane (D) All of these

71.   $\xrightarrow[\text{Pyridine}]{\text{SOCl}_2}$  (A). The product A will be :

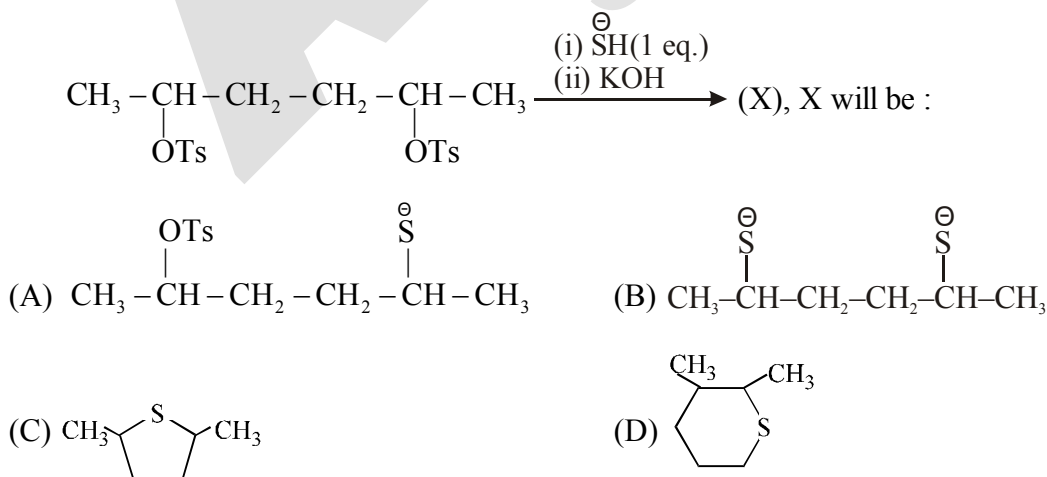
- (A)  (B)  (C)  $\text{H}_2\text{C} = \text{CH}_2$  (D) 

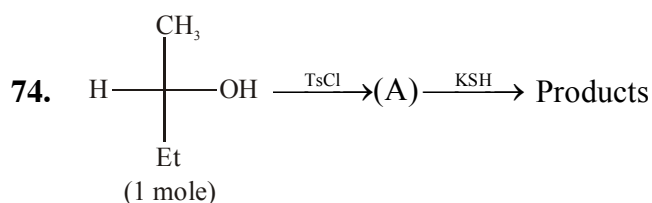
72. Which reaction conditions (reagents) is suitable for the following reaction:



- (A)  $\text{Br}_2 / \text{CCl}_4$  (B)  $\text{SOBr}_2$  (C)  $\text{PBr}_3$  (D)  $\text{HBr} / \text{conc H}_2\text{SO}_4$

73. In the given reaction



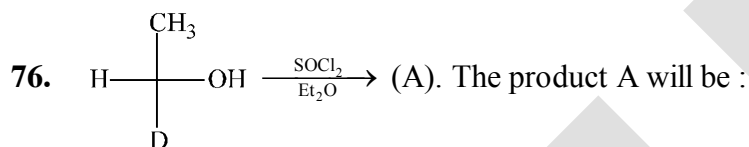


(Assuming all the substrate convert into substitution products containing 0.05 mole of S-configuration) Calculate the percentage of  $\text{S}_{\text{N}}2$  mechanism.

- (A) 90% (B) 80% (C) 70% (D) 95%

75. The reaction of  $\text{SOCl}_2$  on alkanols to form alkyl chlorides gives good yields because

- (A) Alkyl chlorides are immiscible with  $\text{SOCl}_2$   
(B) The other products of the reaction are gaseous and escape out  
(C) Alcohol and  $\text{SOCl}_2$  are soluble in water  
(D) The reaction does not occurs via intermediate formation of an alkyl chloro sulphite

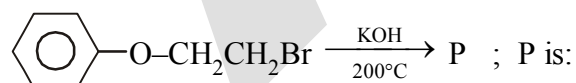


- (A) 
$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{H} - \text{C} - \text{Cl} \\ | \\ \text{D} \end{array}$$
 (B) 
$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{Cl} - \text{C} - \text{H} \\ | \\ \text{D} \end{array}$$
 (C)  $\text{H}_2\text{C} = \text{CH}_2$  (D) 
$$\begin{array}{c} \text{H} \\ \diagup \\ \text{H}_2\text{C} = \text{C} \\ \diagdown \\ \text{D} \end{array}$$

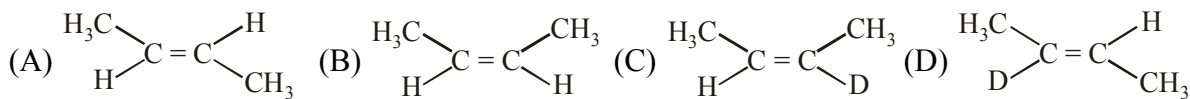
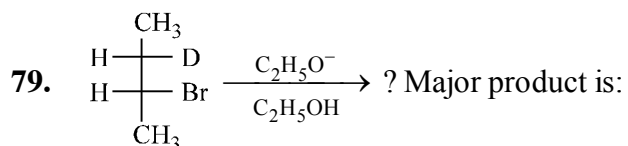
77. In the given pairs, which pair represent correct order of rate dehydrohalogenation reaction.

- (A)  $\text{CH}_3(\text{CH}_2)_4\text{Cl} < (\text{CH}_3)_2\text{CHCH}_2\text{Cl}$  (B)  $\text{CH}_3(\text{CH}_2)_3\text{CH}=\text{CHCl} < (\text{CH}_3)_2\text{CHCH}_2\text{Cl}$   
(C)  $(\text{CH}_3)_2\text{CHI} < (\text{CH}_3)_2\text{CHBr}$  (D)  $\text{CH}_3 - \text{CH}_2 - \text{Cl} < \text{CD}_3 - \text{CD}_2 - \text{Cl}$

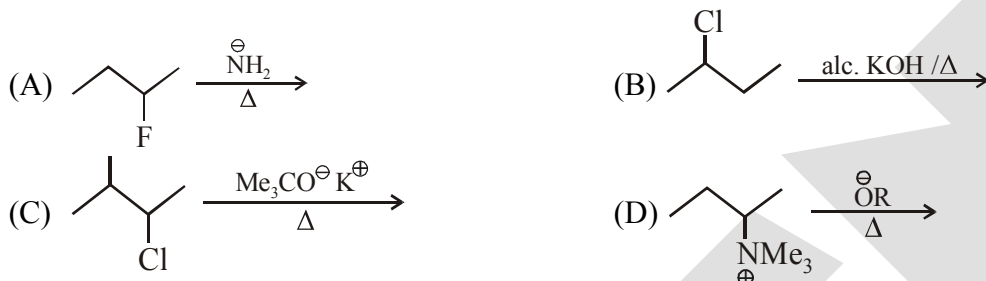
78. The product of the reaction



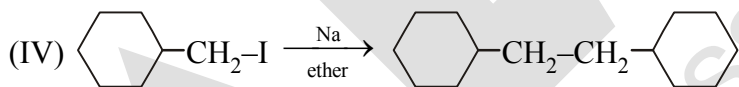
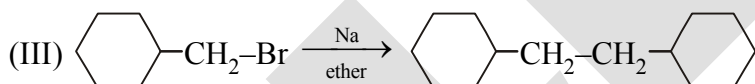
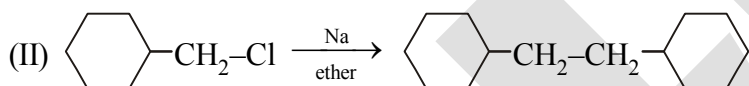
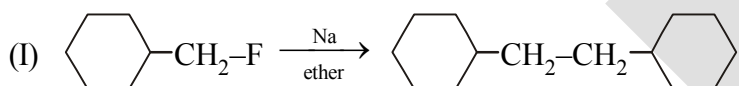
- (A)  $\text{C}_6\text{H}_5\text{OH}$  (B)  $\text{C}_6\text{H}_5\text{OCH}_2\text{CH}_2\text{OH}$   
(C)  (D)  $\text{C}_6\text{H}_5\text{OCH}=\text{CH}_2$



80. Which of following reaction(s) produce Saytzeff product as a major product :



81. The correct order of rate of following Wurtz reactions :

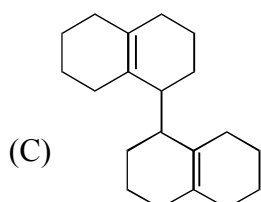
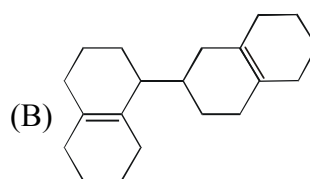
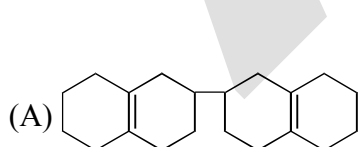
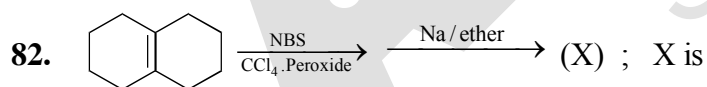


(A) I > II > III > IV

(B) II > I > III > IV

(C) IV > III > II > I

(D) In all rate of Wurtz reaction is same



(D) None of these

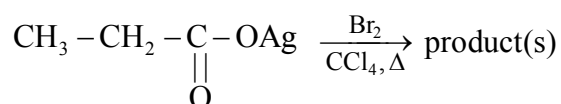
83. Find out the correct order of rate of reaction towards free radical allylic substitution :

- (I)  $\text{CH}_3-\text{CH}=\text{CH}_2$       (II)  $\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}_2$       (III)  $\text{CH}_3-\overset{\text{CH}_3}{\underset{|}{\text{CH}}}-\text{CH}=\text{CH}_2$   
 (A)  $\text{I} > \text{II} > \text{III}$       (B)  $\text{II} > \text{I} > \text{III}$       (C)  $\text{III} > \text{II} > \text{I}$       (D)  $\text{III} > \text{I} > \text{II}$

84. What will be the major product, when 2-methyl butane undergoes bromination in presence of light ?

- (A) 1-Bromo-2-methyl butane      (B) 2-Bromo-2-methyl butane  
 (C) 2-Bromo-3-methyl butane      (D) 1-Bromo-3-methyl butane

85. Which can not be the possible product of the given reaction ?



- (A)  $\text{CH}_3-\text{CH}_2-\text{Br}$       (B)  $\text{CH}_3-\text{CH}_2-\overset{\text{O}}{\underset{||}{\text{C}}}-\text{O}-\text{CH}_2-\text{CH}_3$   
 (C)  $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_3$       (D)  $\text{CH}_3-\text{CH}_2-\text{CH}_3$

86. Choose that alkane which cannot give only one monochloro derivative upon reaction with chlorine in sun light :

- (A)       (B)       (C)       (D) 

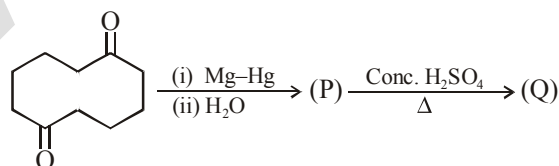
87. 2-chloropentane on halogenation with chlorine gives 2,3, dichloropentane. What will be the structure of free radical species formed in the reaction ?

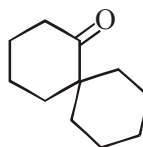
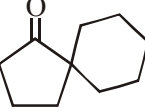
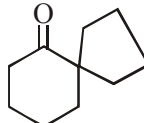
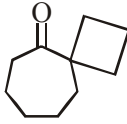
- (A) Tetrahedral      (B) Trigonal planar      (C) Square planar      (D) Pyramidal

88. On mixing a certain alkane with chlorine and irradiating it with ultraviolet light, it forms only one monochloroalkane. This alkane could be -

- (A) neopentane      (B) propane      (C) pentane      (D) isopentane

89. Major product (Q) of following reaction is :

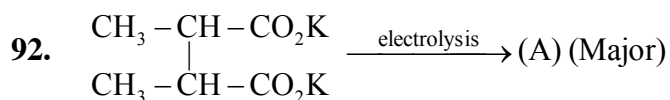
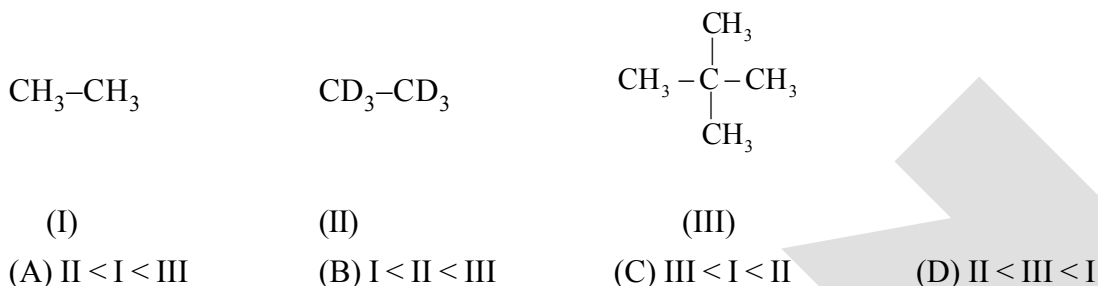


- (A)       (B)       (C)       (D) 

90. 1-Bromo-3-chloro cyclobutane on reaction with 2-equivalent of sodium in ether gives



91. Correct order of rate of photochlorination for following compounds is :



Major product (A) of above reaction :



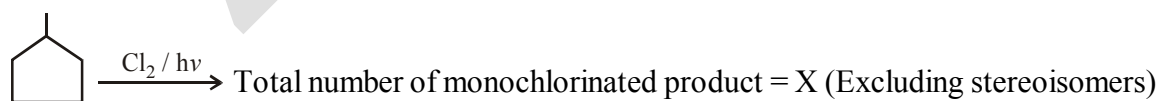
93. During the preparation of ethane by Kolbe's electrolytic method using inert electrode the pH of the electrolyte

- (A) Decreases progressively as the reaction proceeds  
 (B) Increases progressively as the reaction proceeds  
 (C) Remains constant throughout the reaction  
 (D) May decrease if concentration of the electrolytes is not very high

94. When isobutane is chlorinated in the presence of diffused sunlight, then the product formed is :

- (A) Tertiary butyl chloride in major amount  
 (B) Isobutyl chloride in major amount  
 (C) Both 50 % each  
 (D) n-Butyl chloride, isobutyl chloride and sec-butyl chloride are formed

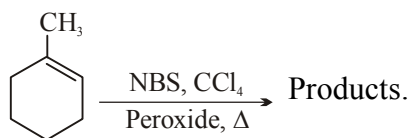
95. Consider the following reactions :



Identify value of X + Y.

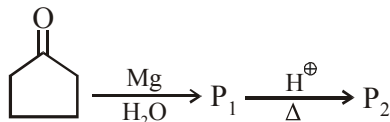
- (A) 8      (B) 9      (C) 11      (D) 10

96. Find out the total no. of products (including stereo) in the given reaction :



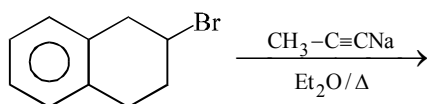
- (A) 8 (B) 9 (C) 10 (D) 11

97. Which of the following is not correct about  $P_2$  :



- (A) It is a spiro compound (B) It is a Ketone  
(C) It can show tautomerism (D) Its double bond equivalent is 4
98. On heating glycerol with excess amount of HI, the product formed is—  
(A) Allyl iodide (B) Isopropyl iodide  
(C) Propylene (D) 1,2,3-tri-iodopropane

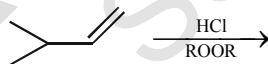
99. In the given reaction:



the products are:

- (A) and (B)   
(C) (D)

100. Major product of the reaction -



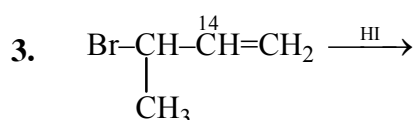
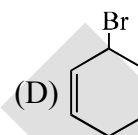
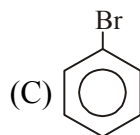
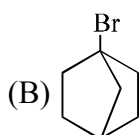
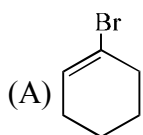
- (A) (B) (C) (D)



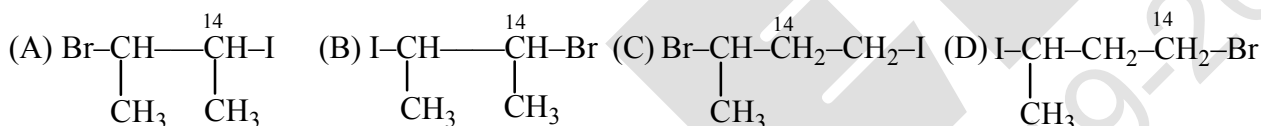
## EXERCISE # II (A)

(Choose the correct option. One or more than one are correct)

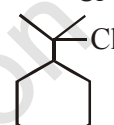
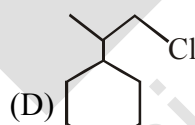
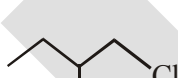
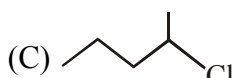
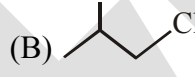
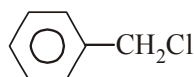
1. Rate of  $S_N2$  depends on :  
 (A) Conc of Nucleophile (B) Conc of substrate  
 (C) Nature of leaving group (D) Nature of solvent
2.  $S_N2$  reaction will be negligible in



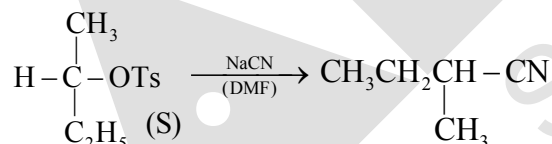
Products which can be obtained during the reaction in good yield :



4. In the given pair in which pair the first compound is more reactive than second towards  $S_N2$  reaction.



5. Consider the given reaction



which of following statements is/are correct for the above reaction.

- (A) Product formation takes place due to the breaking of O-Ts  
 (B) The reaction is  $S_N2$   
 (C) The reaction is  $S_N1$   
 (D) Configuration of product is (R)

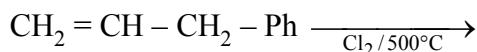
6. Which of the following statements is / are true?
- (A)  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-I}$  will react more readily than  $(\text{CH}_3)_2\text{CHI}$  for  $\text{S}_\text{N}2$  reactions.
- (B)  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-Cl}$  will react more readily than  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-Br}$  for  $\text{S}_\text{N}2$  reaction.
- (C)  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-Br}$  will react more readily than  $(\text{CH}_3)_3\text{C-CH}_2\text{-Br}$  for  $\text{S}_\text{N}2$  reactions
- (D)  $\text{CH}_3\text{-O-C}_6\text{H}_4\text{-CH}_2\text{Br}$  will react more readily than  $\text{NO}_2\text{-C}_6\text{H}_5\text{-CH}_2\text{Br}$  for  $\text{S}_\text{N}2$  reaction

7. Incorrect statement about alkyl halides is / are:
- (A) Tertiary alkyl halides undergo  $\text{S}_\text{N}2$  substitutions
- (B) Alkyl iodides on exposure to sunlight gradually darken
- (C) Photo iodination is irreversible in presence of  $\text{HIO}_3$
- (D) A nucleophilic substitution is most difficult in alkyl iodides

8.  $\text{S}_\text{N}1$  &  $\text{S}_\text{N}2$  is not favourable in

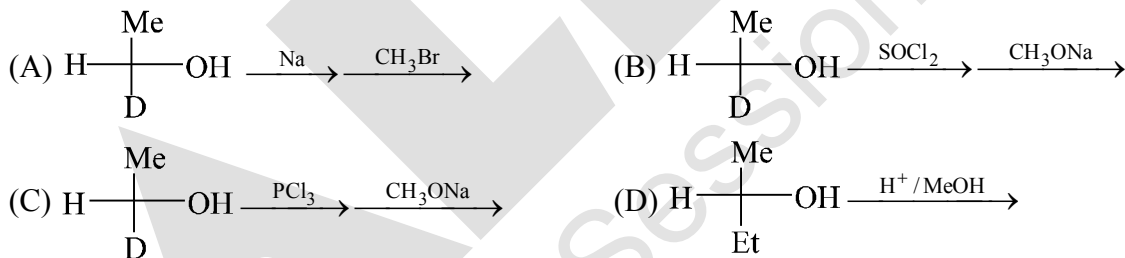


9. Correct statement(s) for the product(s) of following reaction.



- (A) Four different products are formed
- (B) Two optically active products are formed
- (C) The optically active compound formed here can also be made by the reaction of  $\text{HCl}$
- (D) The reaction path is free radical substitution.

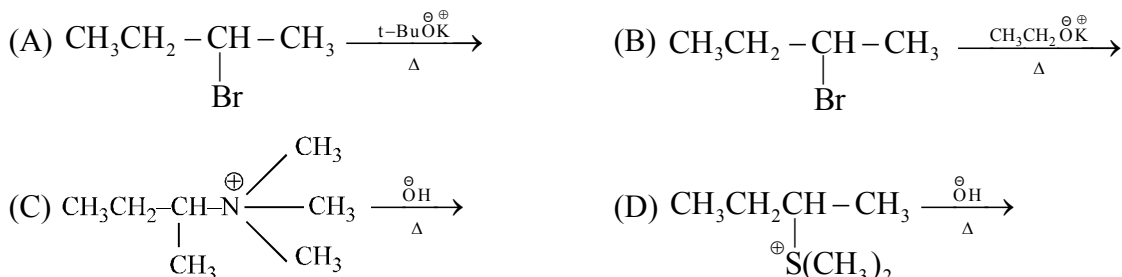
10. In which of the following reaction configuration about chiral C is retained in the final product



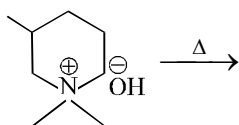
11. A gem dichloride is formed in the reaction :

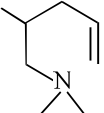
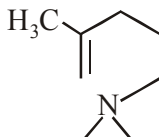


12. In which product formation takes place according to Hoffmann's rule

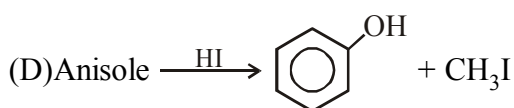
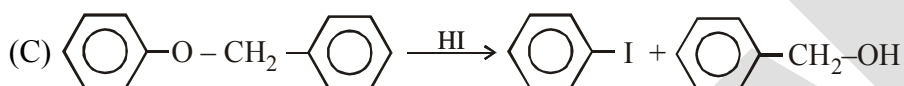


13. Which of following are correct for given reaction

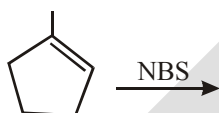


- (A) Major product of reaction is  (B) Major product is   
 (C) The reaction is thermal elimination reaction (D) The reaction is E<sub>2</sub> reaction

14. In which case incorrect products are formed :

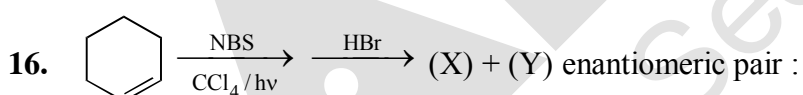


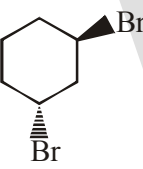
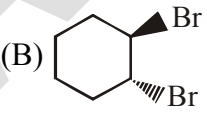
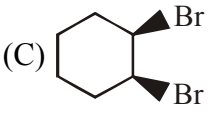
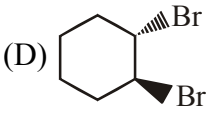
15. In the given reaction :



Find out the correct statement

- (A) It gives total 9 allylic brominated products  
 (B) 6 fractions are obtained on fractional distillation of product mixture  
 (C) Substrate has 7 allylic hydrogens  
 (D) NBS is a brominating agent for allylic positions

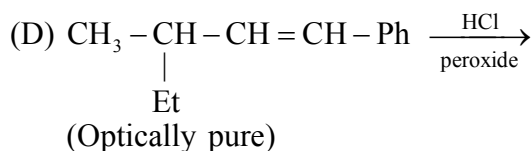
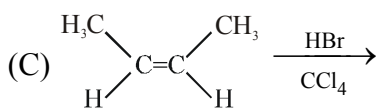
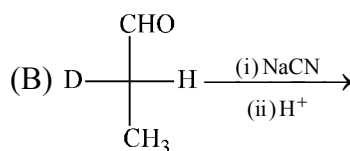
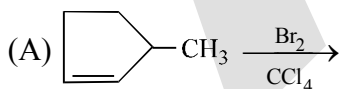


- (A)  (B)  (C)  (D) 

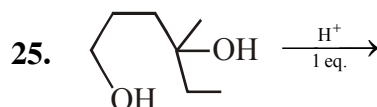
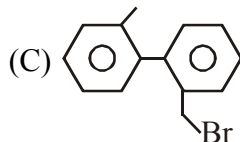
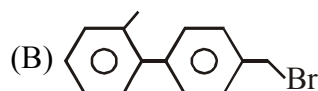
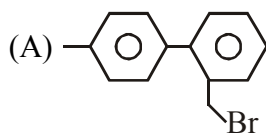
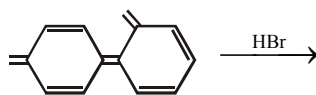
17. Which of the following can be produced by Wurtz reaction in good yield :

- (A)  (B)  (C)  (D) 

18. Products formed when HCl adds to 2,4-hexadiene is :
- (A) 4-chloro-2-hexene (B) 2-chloro-3-hexene  
(C) 2-chloro-4-hexene (D) 1-chloro-2-hexene
19. Correct statement among the following is/are :
- (A) The rate of hydrolysis of tertiary butyl bromide increases by addition of  $\text{Ag}_2\text{O}$   
(B) Aqueous  $\text{Ag}_2\text{O}$  produces nucleophilic  $\text{OH}^-$   
(C) The addition of a small amount of oxygen slows down the photochemical chlorination of methane.  
(D)  $\text{CH}_3\text{CH}_2\text{Cl}$  is more reactive than  $\text{PhCH}_2\text{Cl}$  for bimolecular nucleophilic substitution reaction
20. Incorrect statement among the following is/are :
- (A)  $\text{R-OH}$  with  $\text{NaI}$  in the presence of phosphoric acid gives  $\text{R-I}$ , but not in the absence of phosphoric acid  
(B) 2-methyl propane on chlorination ( $\text{Cl}_2, h\nu$ ) gives 1-chloro-2-methyl propane while bromination ( $\text{Br}_2, h\nu$ ) gives 2-bromo-2-methyl propane  
(C) Usually higher temperature prefers substitution over elimination  
(D) Triphenyl chloromethane cannot be hydrolysed
21. Correct statements among the following is/are :
- (A) Dihaloalkanes having the same type of halogen atoms on same atom are named as alkylidene dihalides  
(B) Dihaloalkanes having the same type of halogen atoms on adjacent atoms are named as alkylene dihalides  
(C) In common name system gem-dihalides are named as alkylidene halide  
(D) In common name system vic-dihalides are named as alkylene halide
22. Which of the following is correct order of nucleophilicity ?
- (A)  $(\text{CH}_3\text{CH}_2)_3\text{N} > \text{pyridine}$  (B)  $\text{HOO}^- > \text{HO}^-$  in DMSO  
(C)  $\text{H}_2\text{S} > \text{H}_2\text{O}$  (D)  $\text{CH}_3\text{O}-\text{C}_6\text{H}_4-\text{O}^- > \text{CH}_3-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{O}^-$
23. Which of following reaction products are diastereomer of each other :



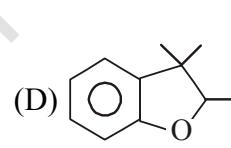
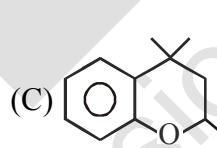
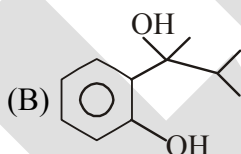
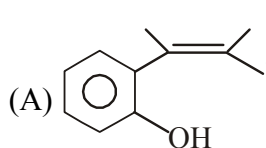
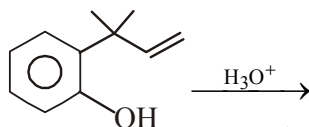
24. Product obtained in given reaction in good yield are :



Correct statements for given reaction :

- (A) Product mixture is resolvable
- (B) Product can be separated by fractional distillation of mixture
- (C) Two products possible & both are optically active
- (D) Products are diastereomer

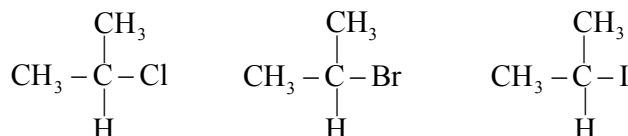
26. Which of the following can be formed during this reaction ?



27. Select **true** statement(s) :

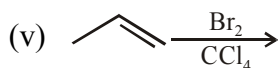
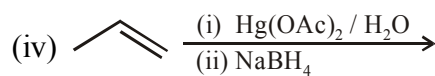
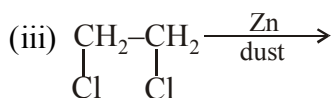
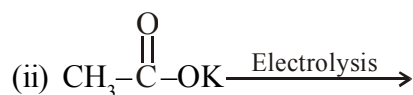
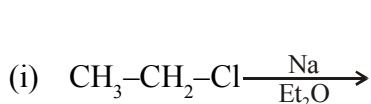
- (A) Cyclopropane decolorizes bromine water
- (B) In general, bromination is more selective than chlorination.
- (C) The 2,4,6-tri-tert, butylphenoxy radical is resistant to dimerization.
- (D) The radical-catalysed chlorination,  $\text{ArCH}_3 \rightarrow \text{ArCH}_2\text{Cl}$ , occurs faster when  $\text{Ar} = \text{phenyl}$  than when  $\text{Ar} = \text{p-nitrophenyl}$ .

28. From left to right, correct statements are :



- (A) Rate of  $\text{S}_{\text{N}}1$  mechanism increases in polar protic solvent
- (B) Rate of  $\text{S}_{\text{N}}2$  mechanism increases in DMSO
- (C) Rate of  $\text{E}_2$  mechanism increases
- (D) Rate of  $\text{E}_1$  mechanism increases

29. Number of following reactions which produces hydrocarbon as major product ?

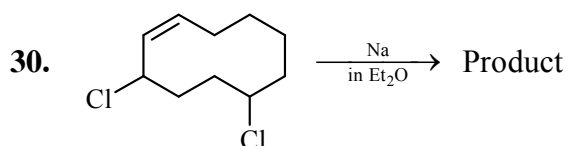


(A) 2

(B) 4

(C) 5

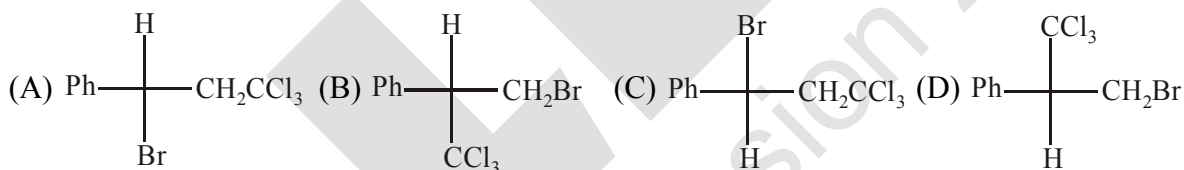
(D) 6



Correct statement is/are :

- (A) odd no. of double bond equivalent in product
- (B) product is bicyclic compound
- (C) product can show geometrical isomerism
- (D) reaction involve carbocation as intermediate

31.  $\text{Ph---CH=CH}_2 + \text{BrCCl}_3 \xrightarrow{\text{Peroxide}}$  Product is :



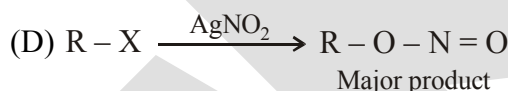
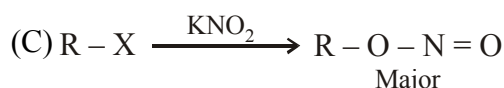
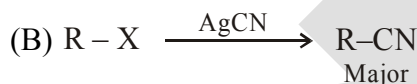
## EXERCISE # II (B)

## Comprehension Type :

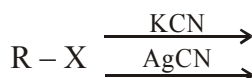
## Paragraph for Q.No. 01 to 02

Groups like CN &  $[-O-\ddot{N}=O]$  possess two nucleophilic centre and are called ambident nucleophiles. Actually cyanide group is hybriide of two contributing structures and therefore can act as nucleophile in two different ways  $[\overset{\ominus}{C}\equiv N \longleftrightarrow :C \equiv N^{\ominus}]$ . Similarly nitrite ion also represents an ambident nucleophile with two different points of linkage  $[O-\ddot{N}=O]$ .

1. Correct option among the following :



2. Incorrect statement



(A) KCN is predominately ionic in nature

(B) AgCN is mainly covalent in nature

(C) In AgCN, carbon is the donor atom

(D) In AgCN nitrogen is the donor atom

3. **Statement-1** : HBr shows antimarkownikoff's addition on propene but not HCl.

**Statement-2** : H-Br is stronger acid than H-Cl.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

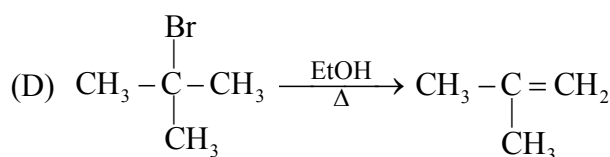
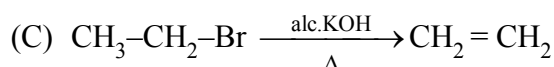
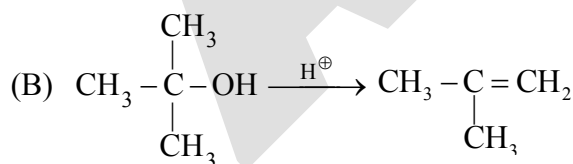
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

4. Match the List I with List II and select the correct answer using the codes given below the Lists.

## List I



## List II

(P) Elimination Reaction

(Q) Carbocation

(R) Carbanion

(S) Free radical

5. Match List I with List II and select the correct answer from the codes given below:

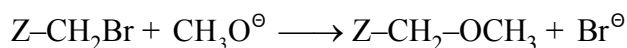
**List I**  
(Reactions)

- (A)  $\text{CH}_3\text{O}-\text{SO}_2\text{CH}_3 + \text{C}_2\text{H}_5\text{O}^-$   
(B)  $\text{CH}_3-\text{CH}_2-\text{I} + \text{PH}_3$   
(C)  $\text{HC}\equiv\text{C}^-\text{Na}^+ + \text{CH}_3-\text{CH}_2-\text{Br}$   
(D)  $\text{CH}_3-\text{Cl} + \text{CH}_3-\text{O}^-$

**List II**  
(Products)

- (P)  $\text{CH}_3-\text{CH}_2-\text{PH}_2$   
(Q)  $\text{CH}_3-\text{O}-\text{C}_2\text{H}_5$   
(R)  $\text{CH}_3-\text{O}-\text{CH}_3$   
(S)  $\text{CH}\equiv\text{C}-\text{CH}_2-\text{CH}_3$

6. Match List-I with List-II for given  $\text{S}_{\text{N}}2$  reaction & select the correct answer from the codes given below



**List-I (Z-)**

- (A)  $\text{H}-$   
(B)  $\text{CH}_3-$   
(C)  $\text{C}_2\text{H}_5-$   
(D)  $\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{CH} \\ \diagup \\ \text{CH}_3 \end{array}-$

**List-II (relative reactivity)**

- (P) 0.1  
(Q) 3  
(R) 1  
(S) 100

7. Match the List I with List II and select the correct answer using the codes given below the Lists.

**List I**

- (A)  $\text{E}_{1\text{CB}}$   
(B) Saytzeff alkene as major product  
(C)  $\text{E}_2$   
(D)  $\text{E}_i$

**List II**

- (P)  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{N}^+-\text{O}^- \\ | \\ \text{CH}_3 \end{array}$   
(Q)  $\text{CH}_3\text{CH}_2\text{CH}_2-\text{O}-\text{C}(=\text{S})-\text{S}-\text{CH}_3$   
(R)  $\begin{array}{c} \text{Cl} \\ | \\ \text{CH}_3-\text{CH}_2-\text{CH}-\text{CH}_3 \end{array}$   
(S)  $\begin{array}{c} \text{C}_6\text{H}_5-\text{CH}_2-\text{CH}-\text{CH}_3 \\ | \\ \text{F} \end{array}$

8. **Column - I**  
(Reactions)

- (A)  $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 \xrightarrow{\text{HBr}}$   
(B)  $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 \xrightarrow{\text{HBr, Peroxide}}$   
(C)  $\text{PhCH}(\text{CH}_3)\text{OH} \xrightarrow{\text{SOCl}_2}$   
(D)  $\text{PhCH}(\text{CH}_3)\text{OH} \xrightarrow{\text{HBr}}$

**Column - II**  
(Characteristics)

- (P) Bimolecular  
(Q) Carbocation intermediate  
(R) Regioselective  
(S) Racemic modification  
(T) Stereospecific reaction



## 9. Column - I

(Statements)

- (A) Reactions are concerted  
 (B)  $\text{CH}_3\text{X}$  cannot react  
 (C)  $3^\circ \text{R-X} > 2^\circ \text{R-X} > 1^\circ \text{R-X}$   
 (D)  $\text{R-I}$  reacts faster than  $\text{R-Cl}$

## Column - II

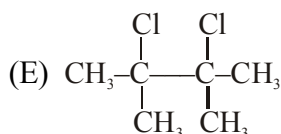
(Consistent path of reaction)

- (P)  $\text{S}_{\text{N}}1$   
 (Q)  $\text{S}_{\text{N}}2$   
 (R)  $\text{E}1$   
 (S)  $\text{E}2$

10. Each of the compounds in column A is subjected to further chlorination. Match the following for them :

## Column - A

- (A)  $\text{CHCl}_2\text{-CH}_2\text{-CH}_3$   
 (B)  $\text{CH}_2\text{Cl-CHCl-CH}_3$   
 (C)  $\text{CH}_2\text{Cl-CH}_2\text{-CH}_2\text{-Cl}$   
 (D)  $\text{CH}_3\text{-CCl}_2\text{-CH}_3$



## Column - B

- (P) Optically active original compound  
 (Q) Only one trichloro product  
 (R) Three trichloro product.  
 (S) Four trichloro product  
 (T) At least one of the trichloro product is optically active  
 (U) Two trichloro products.

## 11. Column - I

(Intermediate)

- (A) Carbocation  
 (B) Carbanion  
 (C) Free radical  
 (D) Octet complete in one of the intermediate

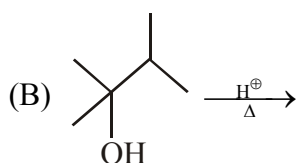
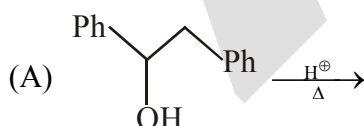
## Column - II

- (P) Kolbey Electrolysis  
 (Q) Wurtz reaction  
 (R) Dehydration of alcohol  
 (S) Monocarboxylic acid with sodalime

12. Match the column

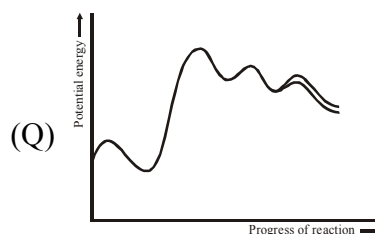
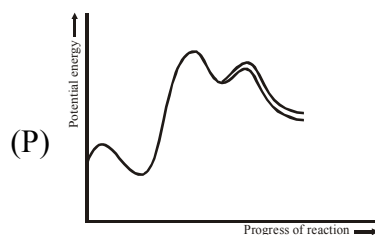
## Column-I

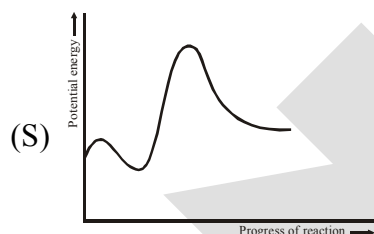
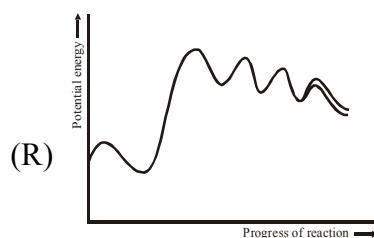
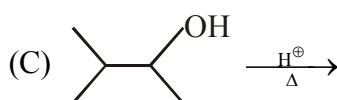
(Reaction)



## Column-II

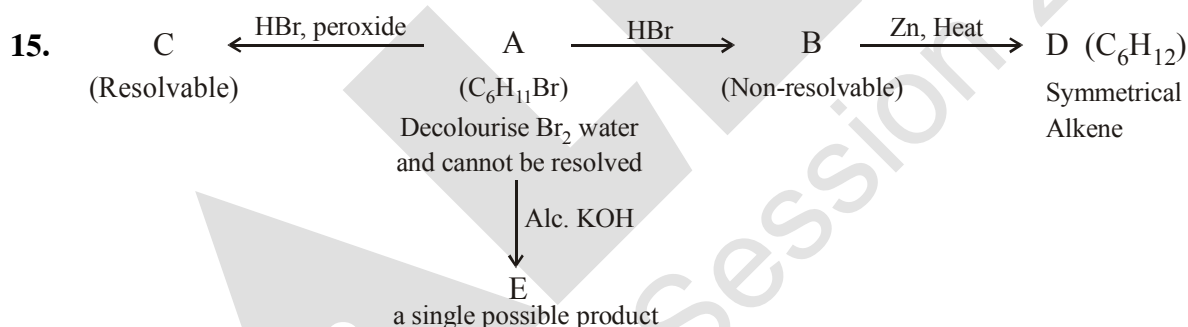
(Potential energy curve)





### Subjective Type :

13. RCl is treated with Li in ether to form R – Li, R – Li reacts with water to form isopentane. R – Cl also reacts with sodium to form 2, 7-dimethyloctane. What is the structure of R – Cl.
14. A chloroderivative 'X' on reduction gave a hydrocarbon with five carbon atoms in the molecule. When X is dissolved in ether and treated with sodium, 2, 2, 5, 5-tetramethyl hexane is obtained. What is compound X.



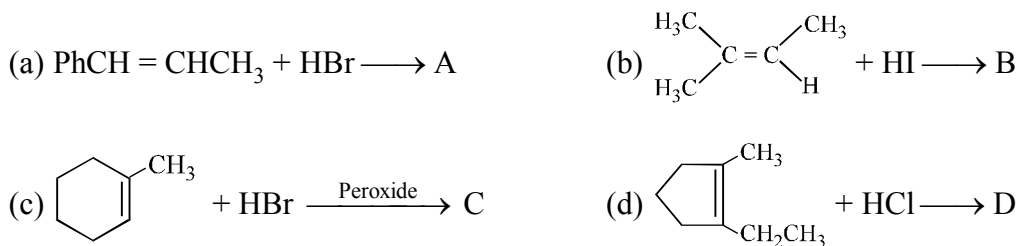
Identify A, C & E in the sequence of reaction.

16. With the help of following data show HBr exhibits the peroxide effect.

|     | $\Delta H_1^0/\text{kJ mol}^{-1}$                                                                | $\Delta H_2^0/\text{kJ mol}^{-1}$                                                                           |
|-----|--------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------|
| H-X | $\dot{\text{X}} + \text{CH}_2 = \text{CH}_2 \rightarrow \text{XCH}_2 - \dot{\text{C}}\text{H}_2$ | $\text{XCH}_2 - \dot{\text{C}}\text{H}_2 + \text{H-X} \rightarrow \text{XCH}_2\text{CH}_3 + \dot{\text{X}}$ |
|     | $\downarrow$                                                                                     |                                                                                                             |
| HCl | -67                                                                                              | + 12.6                                                                                                      |
| HBr | -25.1                                                                                            | - 50.2                                                                                                      |
| HI  | +46                                                                                              | -117.1                                                                                                      |

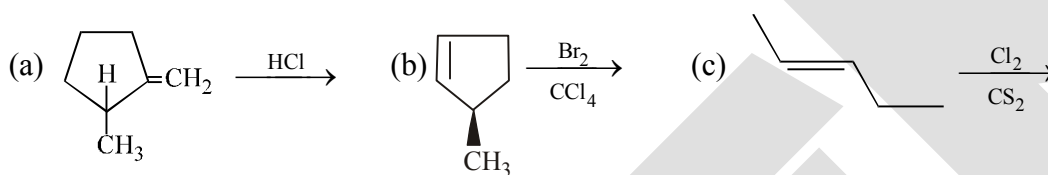
17. Write all the monochlorinated products (including stereo) of isohexane.

18. What are the products of the following reactions ?



19. It required 0.7 g of a hydrocarbon (A) to react completely with  $\text{Br}_2$  (2.0 g) and form a non resolvable product. On treatment of (A) with  $\text{HBr}$  it yielded monobromo alkane (B). The same compound (B) was obtained when (A) was treated with  $\text{HBr}$  in presence of peroxide. Write down the structure formula of (A) and (B) and explain the reactions involved.

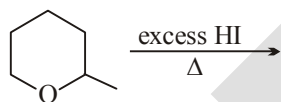
20. Complete following reaction :



21.  $\text{CH}_3\text{--CH}_2\text{I}$  reacts more rapidly with strong base in comparison to  $\text{CD}_3\text{CH}_2\text{I}$ .

22.  $\text{CH}\equiv\text{C--CH}_2\text{--CH=CH}_2$ , adds up  $\text{HBr}$  to give  $\text{CH}\equiv\text{C--CH}_2\text{--CHBr--CH}_3$  while  $\text{CH}\equiv\text{C--CH=CH}_2$  adds up  $\text{HBr}$  to give  $\text{CH}_2=\underset{\text{Br}}{\text{C}}\text{--CH=CH}_2$

23. Predict the product(s) and write the mechanism of the given reaction :



24. What are the products of the following reactions?

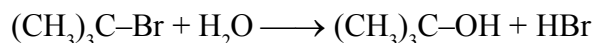


25. A primary alkyl bromide (A),  $\text{C}_4\text{H}_9\text{Br}$ , reacted with alcoholic  $\text{KOH}$  to give compound (B). Compound (B) reacted with  $\text{HBr}$  to give an isomer of (A). When (A) was reacted with sodium metal it gave compound (D),  $\text{C}_8\text{H}_{18}$ , which was different from the compound produced when n-butyl bromide was reacted with sodium. Draw the structure of (A) and write equations for all the reactions.

26. In study of chlorination of propane four products (A,B,C,D) of molecular formula  $\text{C}_3\text{H}_7\text{Cl}_2$  were obtained. On further chlorination of the above products A gave one trichloro product, B gave two whereas C and D gave three each. When optically active C was chlorinated one of trichloro propanes was optically active and remaining two were optically inactive. Identify the structures of A, B, C and D, and explain formation of products.

EXERCISE # III (J-MAINS)

1. Following reaction :



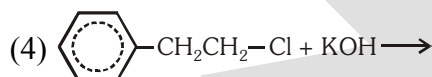
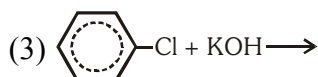
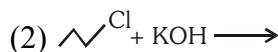
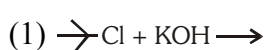
is an example of-

[AIEEE-2002]

- (1) Elimination reaction (2) Free radical substitution  
(3) Nucleophilic substitution (4) Electrophilic substitution

2.  $\text{SN}^1$  reaction is feasible in-

[AIEEE-2002]



3. Bottles containing  $\text{C}_6\text{H}_5\text{I}$  and  $\text{C}_6\text{H}_5\text{CH}_2\text{I}$  lost their original labels. They were labelled A and B for testing. A and B were separately taken in a test tube and boiled with  $\text{NaOH}$  solution. The end solution in each tube was made acidic with dilute  $\text{HNO}_3$  and then some  $\text{AgNO}_3$  solution was added. Substance B gave a yellow precipitate. Which one of the following statements is true for this experiment.

[AIEEE-2003]

- (1) A was  $\text{C}_6\text{H}_5\text{I}$  (2) A was  $\text{C}_6\text{H}_5\text{CH}_2\text{I}$   
(3) B was  $\text{C}_6\text{H}_5\text{I}$  (4) Addition of  $\text{HNO}_3$  was unnecessary

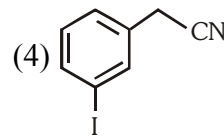
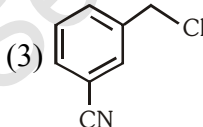
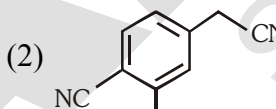
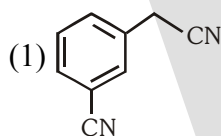
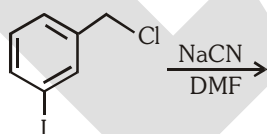
4. The compound formed on heating chlorobenzene with chloral in the presence of concentrated sulphuric acid is-

[AIEEE-2004]

- (1) Gammex (2) DDT (3) Freon (4) Hexa chloro ethane

5. The structure of the major product formed in the following reaction is :

[AIEEE-2006]

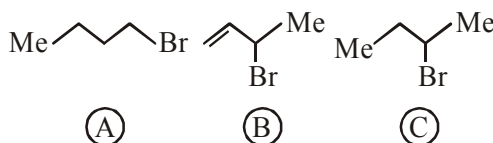


6. Which of the following on heating with aqueous  $\text{KOH}$ , produces acetaldehyde ? [AIEEE-2009]

- (1)  $\text{CH}_2\text{ClCH}_2\text{Cl}$  (2)  $\text{CH}_3\text{CHCl}_2$  (3)  $\text{CH}_3\text{COCl}$  (4)  $\text{CH}_3\text{CH}_2\text{Cl}$

7. Consider the following bromides :-

[AIEEE-2010]



The correct order of  $\text{S}_\text{N}^1$  reactivity is

- (1)  $\text{A} > \text{B} > \text{C}$  (2)  $\text{B} > \text{C} > \text{A}$  (3)  $\text{B} > \text{A} > \text{C}$  (4)  $\text{C} > \text{B} > \text{A}$

8. In  $S_N^2$  reactions, the correct order of reactivity for the following compounds : [JEE(Main)-2014]  
 $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{CH}_2\text{Cl}$ ,  $(\text{CH}_3)_2\text{CHCl}$  and  $(\text{CH}_3)_3\text{CCl}$  is :

- (1)  $\text{CH}_3\text{CH}_2\text{Cl} > \text{CH}_3\text{Cl} > (\text{CH}_3)_2\text{CHCl} > (\text{CH}_3)_3\text{CCl}$   
 (2)  $(\text{CH}_3)_2\text{CHCl} > \text{CH}_3\text{CH}_2\text{Cl} > \text{CH}_3\text{Cl} > (\text{CH}_3)_3\text{CCl}$   
 (3)  $\text{CH}_3\text{Cl} > (\text{CH}_3)_2\text{CHCl} > \text{CH}_3\text{CH}_2\text{Cl} > (\text{CH}_3)_3\text{CCl}$   
 (4)  $\text{CH}_3\text{Cl} > \text{CH}_3\text{CH}_2\text{Cl} > (\text{CH}_3)_2\text{CHCl} > (\text{CH}_3)_3\text{CCl}$

9. In a nucleophilic substitution reaction : [JEE(Main)-On-Line-2014]



which one of the following undergoes complete inversion of configuration?

- (1)  $\text{C}_6\text{H}_5\text{CCH}_3\text{C}_6\text{H}_5\text{Br}$  (2)  $\text{C}_6\text{H}_5\text{CHCH}_3\text{Br}$   
 (3)  $\text{C}_6\text{H}_5\text{CHC}_6\text{H}_5\text{Br}$  (4)  $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$

10. The major product obtained in the photo catalysed bromination of 2-methylbutane is :-

- (1) 2-bromo-2-methylbutane  
 (2) 2-bromo-3-methylbutane  
 (3) 1-bromo-2-methylbutane  
 (4) 1-bromo-3-methylbutane

[JEE(Main)-On-Line-2014]

11. In the presence of peroxide,  $\text{HCl}$  and  $\text{HI}$  do not give anti-Markownikoff's addition to alkenes because :- [JEE(Main)-On-Line-2014]

- (1) All the steps are exothermic in  $\text{HCl}$  and  $\text{HI}$   
 (2) One of the steps is endothermic in  $\text{HCl}$  and  $\text{HI}$   
 (3)  $\text{HCl}$  is oxidizing and the  $\text{HI}$  is reducing  
 (4) Both  $\text{HCl}$  and  $\text{HI}$  are strong acids

12. The major product formed when 1,1,1 - trichloro - propane is treated with aqueous potassium hydroxide is : [JEE(Main)-On-Line-2014]

- (1) 2 - Propanol (2) Propionic acid (3) Propyne (4) 1 - Propanol

13. The synthesis of alkyl fluoride is best accomplished by : [JEE(Main)-2015]

- (1) Finkelstein reaction (2) Swarts reaction  
 (3) Free radical fluorination (4) Sandmeyer's reaction

14. 2-chloro-2-methylpentane on reaction with sodium methoxide in methanol yields :

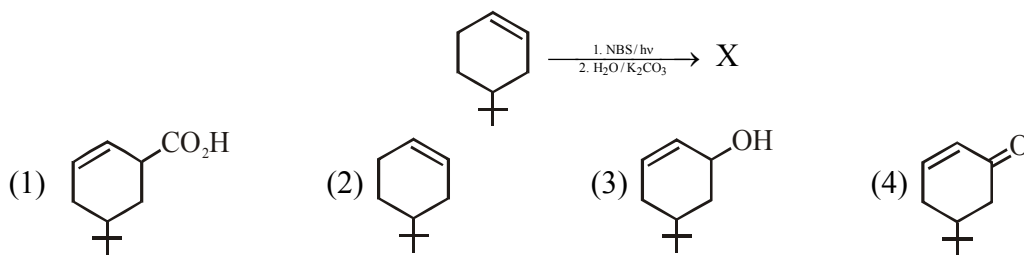
- (1)  $\text{C}_2\text{H}_5\text{CH}_2\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{OCH}_3$  (2)  $\text{C}_2\text{H}_5\text{CH}_2\overset{\text{CH}_3}{\text{C}}=\text{CH}_2$  (3)  $\text{C}_2\text{H}_5\text{CH}_2=\overset{\text{CH}_3}{\text{C}}-\text{CH}_3$

[JEE-MAIN-2016]

- (1) (1) and (2) (2) All of these (3) (1) and (3) (4) (3) only

15. The product of the reaction given below is :

[JEE-MAIN-2016]



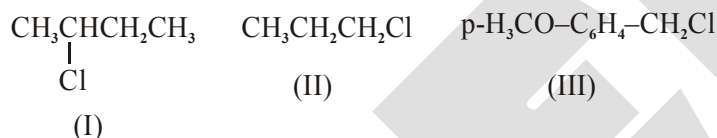
16. The reaction of propene with HOCl ( $\text{Cl}_2 + \text{H}_2\text{O}$ ) proceeds through the intermediate :

[JEE-MAIN-2016]

- (1)  $\text{CH}_3\text{-CHCl-CH}_2^+$
- (2)  $\text{CH}_3\text{-CH}^+\text{-CH}_2\text{-OH}$
- (3)  $\text{CH}_3\text{-CH}^+\text{-CH}_2\text{-Cl}$
- (4)  $\text{CH}_3\text{-CH(OH)-CH}_2^+$

17. The increasing order of the reactivity of the following halides for the  $\text{S}_{\text{N}}1$  reaction is :

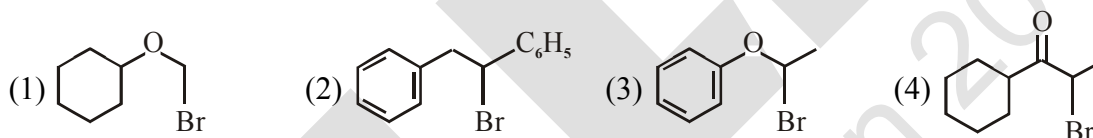
[JEE-MAIN-2017]



- (1) (III) < (II) < (I)
- (2) (II) < (I) < (III)
- (3) (I) < (III) < (II)
- (4) (II) < (III) < (I)

18. Which of the following, upon treatment with tert-BuONa followed by addition of bromine water, fails to decolourize the colour of bromine ?

[JEE-MAIN-2017]



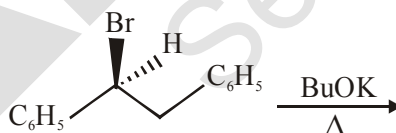
19. 3-Methyl-pent-2-ene on reaction with HBr in presence of peroxide forms an addition product. The number of possible stereoisomers for the product is :

[JEE-MAIN-2017]

- (1) Six
- (2) Zero
- (3) Two
- (4) Four

20. The major product obtained in the following reaction is :

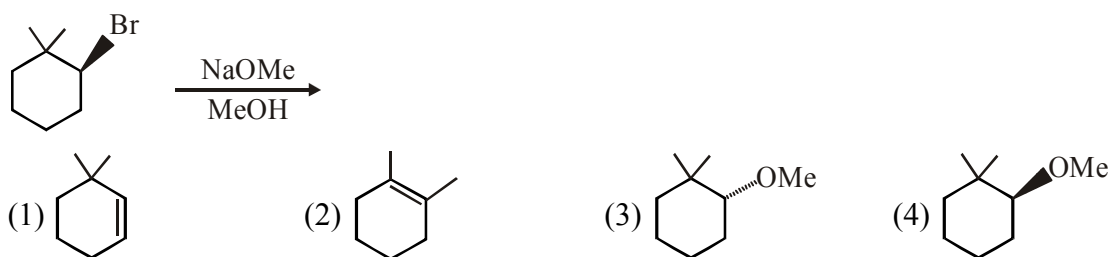
[JEE-MAIN-2017]



- (1)  $(\pm)\text{C}_6\text{H}_5\text{CH}(\text{O}^t\text{Bu})\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$
- (2)  $\text{C}_6\text{H}_5\text{CH=CHC}_6\text{H}_5$
- (3)  $(+)\text{C}_6\text{H}_5\text{CH}(\text{O}^t\text{Bu})\text{CH}_2\text{H}_5$
- (4)  $(-)\text{C}_6\text{H}_5\text{CH}(\text{O}^t\text{Bu})\text{CH}_2\text{C}_6\text{H}_5$

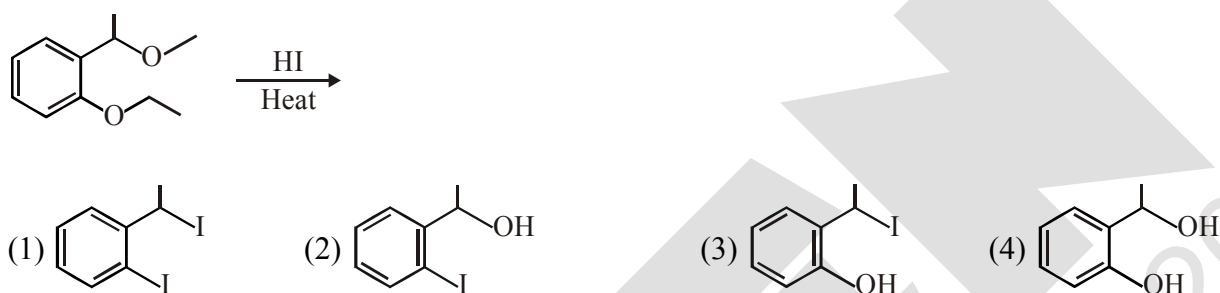
21. The major product of the following reaction is :

[JEE-MAIN-2018]



22. The major product formed in the following reaction is :

[JEE-MAIN-2018]

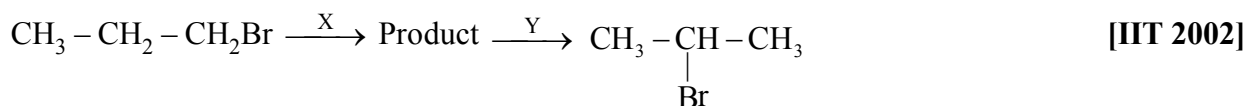


EXERCISE # IV (A) (J-ADVANCE OBJECTIVE)

- Chlorination of toluene in the presence of light and heat followed by treatment with aqueous NaOH gives : [IIT 1990]  
 (A) o-cresol (B) p-cresol  
 (C) 2,4-dihydroxytoluene (D) Benzoic acid
- Aryl halides are less reactive towards nucleophilic substitution reaction as compared to alkyl halides due to [IIT 1990]  
 (A) The formation of less stable carbonium ion  
 (B) Resonance stabilization  
 (C) The inductive effect  
 (D)  $sp^2$  hybridised carbon attached to the halogen
- 1-Chlorobutane on reaction with alcoholic potash gives : [IIT 1991]  
 (A) 1-butene (B) 1-butanol (C) 2-butene (D) 2-butanol
- The products of reaction of alcoholic  $AgNO_2$  with ethyl bromide are [IIT 1991]  
 (A) Ethane (B) Ethyl nitrite (C) Nitroethane (D) Ethyl alcohol
- Arrange the following compounds in order of increasing dipole moment [IIT 1996]  
 Toluene m-dichlorobenzene o-dichlorobenzene p-dichlorobenzene  
 I II III IV  
 (A)  $I < IV < II < III$  (B)  $IV < I < II < III$  (C)  $IV < I < III < II$  (D)  $IV < II < I < III$
- $(CH_3)_3CMgCl$  reaction with  $D_2O$  produces: [IIT 1997]  
 (A)  $(CH_3)_3CD$  (B)  $(CH_3)_3OD$  (C)  $(CD_3)_3CD$  (D)  $(CH_3)_3OD$
- Benzyl chloride ( $C_6H_5CH_2Cl$ ) can be prepared from toluene by chlorination with: [IIT 1998]  
 (A)  $SO_2Cl_2$  (B)  $SOCl_2$  (C)  $Cl_2, (h\nu)$  (D)  $NaOCl$
- The order of reactivity of the following alkyl halides for a  $S_N2$  reaction is: [IIT 2000]  
 (A)  $RF > RC > R-Br > R-I$  (B)  $R-F > R-Br > R-Cl > R-I$   
 (C)  $R-Cl > R-Br > RF > RI$  (D)  $R-I > RBr > R-Cl > R-F$
- Which of the following has the highest nucleophilicity? [IIT 2000]  
 (A)  $F^-$  (B)  $OH^-$  (C)  $CH_3^-$  (D)  $NH_2^-$
- An  $S_N2$  reaction at an asymmetric carbon of a compound always gives. [IIT 2001]  
 (A) an enantiomer of the substance (B) a product with opposite optical rotation  
 (C) a mixture of diastereomers (D) a single stereoisomer
- The compound that will react most readily with NaOH to form methanol is [IIT 2001]  
 (A)  $(CH_3)_4N^+I^-$  (B)  $CH_3OCH_3$  (C)  $(CH_3)_3S^+I^-$  (D)  $(CH_3)_3CCl$

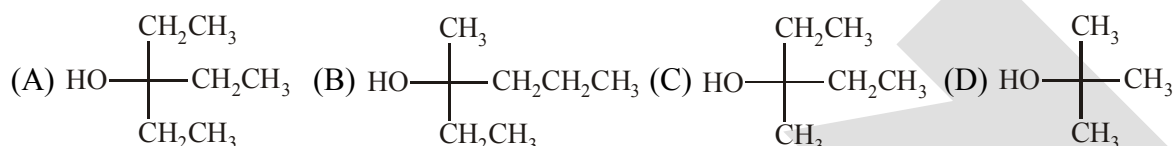


12. Identify the set of reagents / reaction conditions 'X' and 'Y' in the following set of transformation:

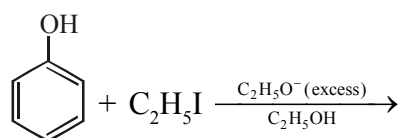


- (A) X = dilute aqueous NaOH, 20°C; Y = HBr / acetic acid, 20°C  
 (B) X = concentrated alcoholic NaOH, 80°C; Y = HBr / acetic acid 20°C  
 (C) X = dilute aqueous NaOH, 20°C; Y = Br<sub>2</sub> / CHCl<sub>3</sub>, 0°C  
 (D) X = concentrated alcoholic NaOH, 80°C; Y = Br<sub>2</sub>/CHCl<sub>3</sub>, 0°C

13. CH<sub>3</sub>MgBr + Ethyl ester → which can be formed as product. (excess) [IIT 2003]

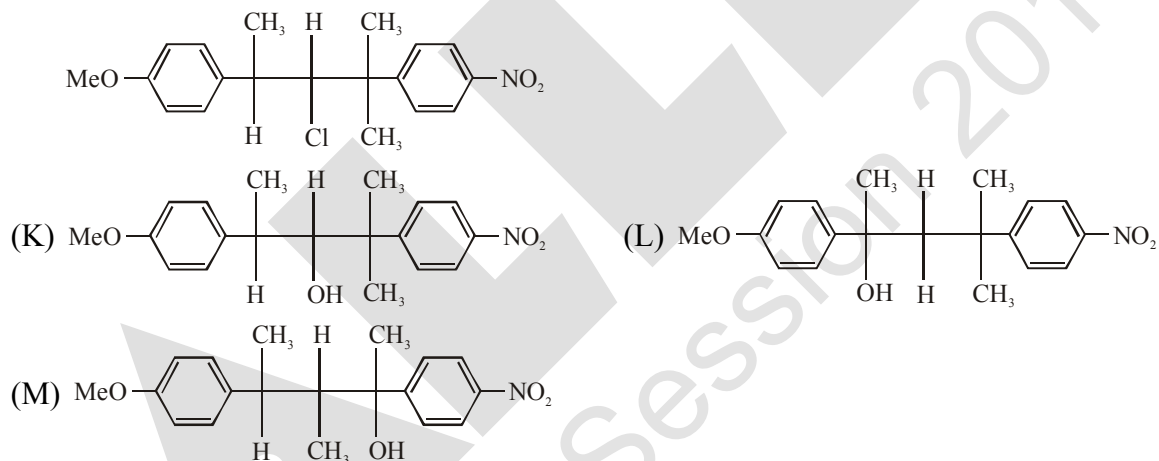


14. The product of following reaction is [IIT 2003]



- (A) C<sub>6</sub>H<sub>5</sub>OC<sub>2</sub>H<sub>5</sub> (B) C<sub>2</sub>H<sub>5</sub>OC<sub>2</sub>H<sub>5</sub> (C) C<sub>6</sub>H<sub>5</sub>OC<sub>6</sub>H<sub>5</sub> (D) C<sub>6</sub>H<sub>5</sub>I

15. The following compound on hydrolysis in aqueous acetone will give: [IIT 2005]



It mainly gives

- (A) K and L (B) Only K (C) L and M (D) Only M

16. Match the following: [IIT 2006]

#### Column I

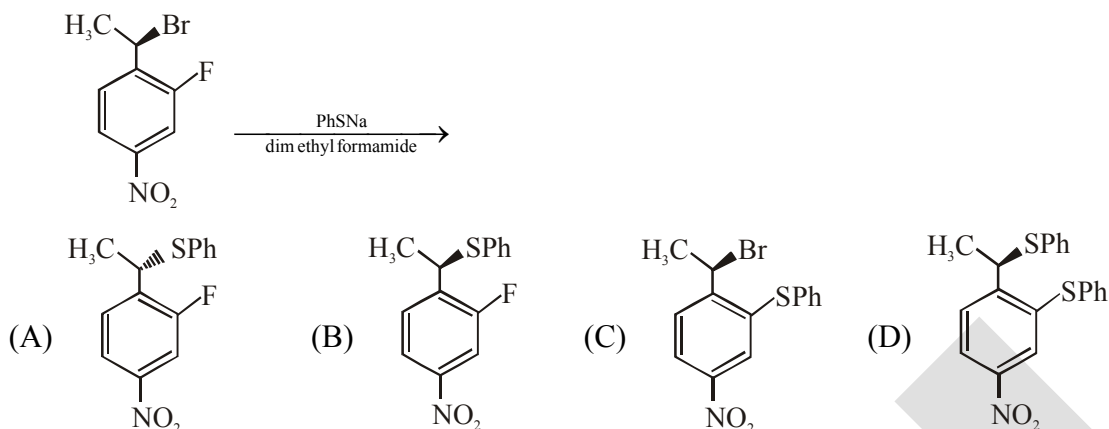
- (A) CH<sub>3</sub>-CHBr-CD<sub>3</sub> on treatment with alc. KOH gives CH<sub>2</sub>=CH-CD<sub>3</sub> as a major product.  
 (B) Ph-CHBr-CH<sub>3</sub> reacts faster than Ph-CHBr-CD<sub>3</sub>.  
 (C) Ph-CD<sub>2</sub>-CH<sub>2</sub>Br on treatment with C<sub>2</sub>H<sub>5</sub>OD/C<sub>2</sub>H<sub>5</sub>O<sup>-</sup> gives Ph-CD=CH<sub>2</sub> as the major product.  
 (D) PhCH<sub>2</sub>CH<sub>2</sub>Br and PhCD<sub>2</sub>CH<sub>2</sub>Br react with same rate.

#### Column II

- (P) E1 reaction  
 (Q) E2 reaction  
 (R) E1cb reaction  
 (S) First order reaction

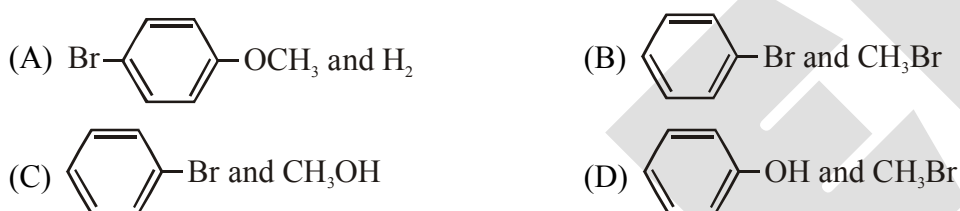
17 The major product of the following reaction is

[IIT 2008]



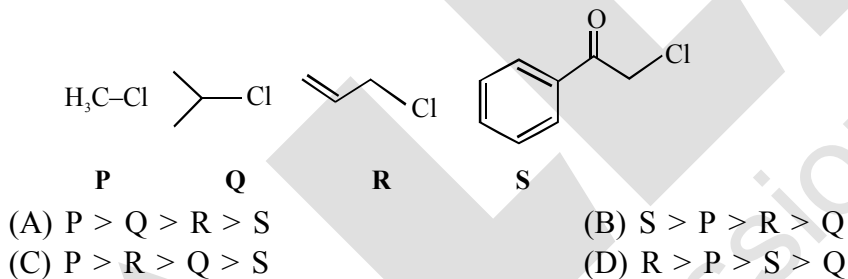
18 In the reaction  $\xrightarrow{\text{HBr}}$  the products are

[IIT 2010]



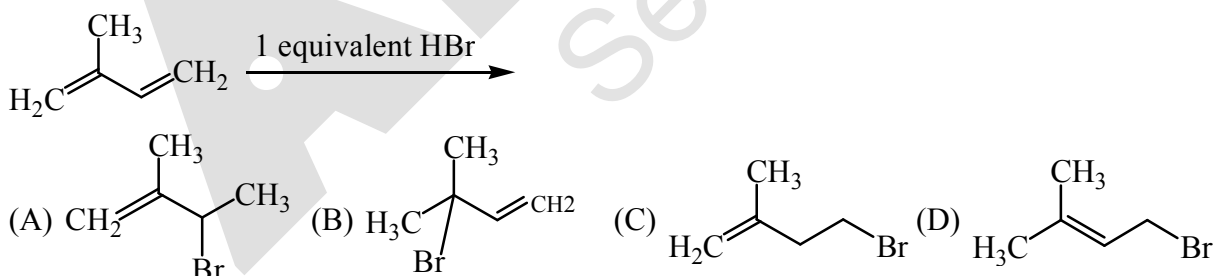
19. KI in acetone, undergoes  $S_N2$  reaction with each of P, Q, R and S. The rates of the reaction vary as -

[IIT 2013]

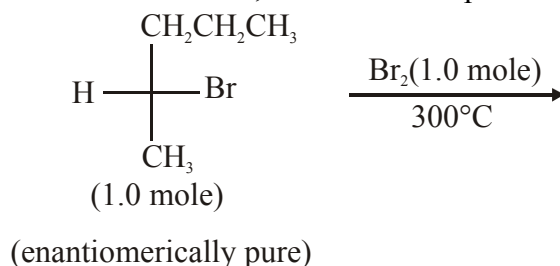


20. In the following reaction, the major product is -

[IIT 2015]

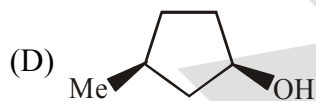
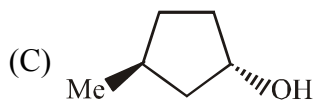
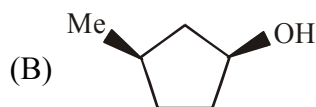
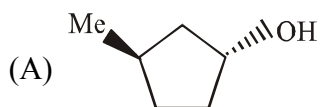
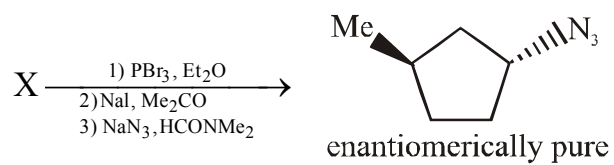


21. In the following monobromination reaction, the number of possible chiral products is [IIT 2016]



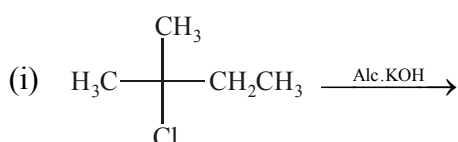
22. In the following reaction sequence, the correct structure(s) of X is (are)

[IIT-2018]

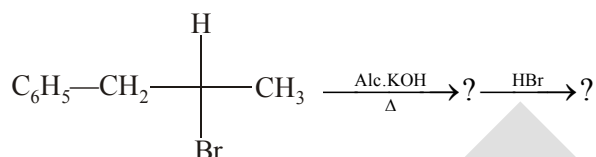


EXERCISE # IV (B) (J-ADVANCE SUBJECTIVE)

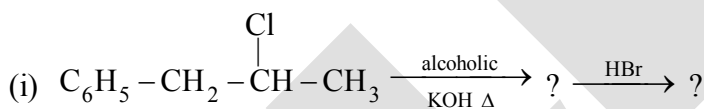
- Fill in the blanks :
  - Butane nitrile can be prepared by heating \_\_\_\_\_ with alcoholic KCN. [IIT 1992]
  - Amongst three isomers of nitrophenol, the one that is least soluble in water is \_\_\_\_\_. [IIT 1992]
- Arrange the following in order of their
  - Increasing basicity  
 $\text{H}_2\text{O}$ ,  $\text{OH}^-$ ,  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{O}^-$
  - Increasing reactivity in nucleophilic substitution reactions  
 $\text{CH}_3\text{F}$ ,  $\text{CH}_3\text{I}$ ,  $\text{CH}_3\text{Br}$ ,  $\text{CH}_3\text{Cl}$  [IIT 1992]
- Write the structures of the major organic product expected from each of the following reactions: [IIT 1992]



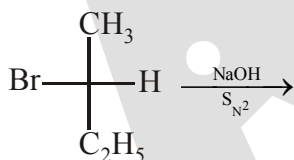
- Identify the major product in the following reaction. [IIT 1993]



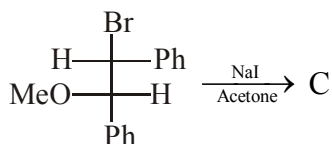
- Identify the major product in the following reactions : [IIT 1993]



- Aryl halides are less reactive than alkyl halides towards nucleophilic reagents. Give reason. [IIT 1994]
- Draw the stereochemical structure of product in the following reaction. [IIT 1994]



- Optically active 2-iodobutane on treatment with NaI in acetone gives a product which does not show optical activity. Explain briefly. [IIT 1995]
- An alkyl halide X of formula  $\text{C}_6\text{H}_{13}\text{Cl}$  on treatment with potassium tertiary butoxide gives two isomeric alkenes Y and Z ( $\text{C}_6\text{H}_{12}$ ). Both alkenes on hydrogenation give 2,3-dimethylbutane. Predict the structures of X, Y and Z. [IIT 1996]
- Predict the structure of the intermediates/products in the following reaction sequence – [IIT 1996]



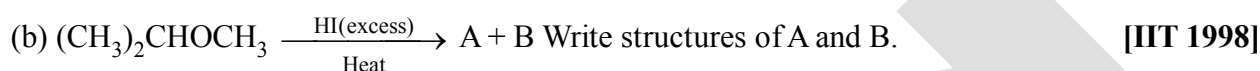
11. Which of the following is the correct method for synthesising methyl-t-butyl ether and why?



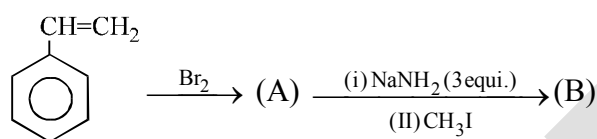
12. Write the structures of the products: [IIT 1998]



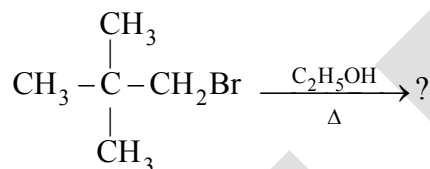
13. (a)  $\text{C}_6\text{H}_5\text{CH}_2\overset{\text{C}_6\text{H}_5}{\underset{\text{CHCl}}{\text{C}}} \xrightarrow[\text{Heat}]{\text{alc. KOH}} \text{A} + \text{B}$  Write structures of (A) and (B).



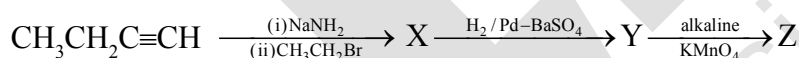
14. Complete the following reaction with appropriate structures of products/reagents. [IIT 1998]



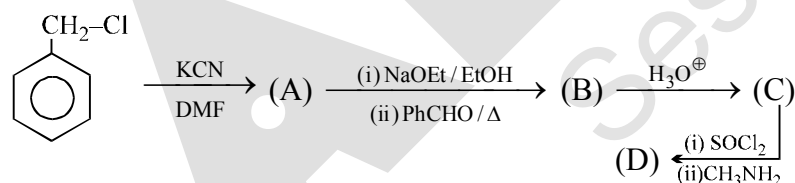
15. What would be major product? [IIT 2000]



16. Identify X, Y and Z in the following synthetic scheme and write their structures [IIT 2002]

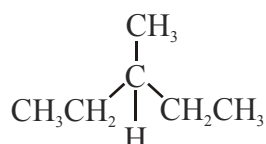


17. Give major products A, B, C and D in following reaction sequence. [IIT 2004]



18. The total number of alkenes possible by dehydrobromination of 3-bromo-3-cyclopentylhexane using alcoholic KOH is [IIT 2011]

19. The maximum number of isomers (including stereoisomers) that are possible on mono-chlorination of the following compounds, is [IIT 2011]



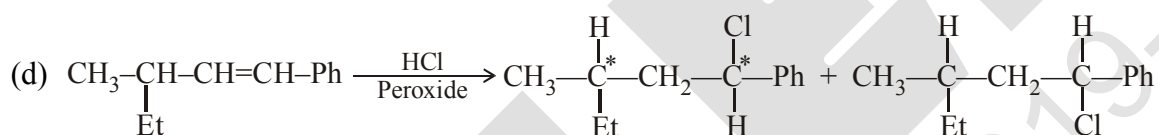
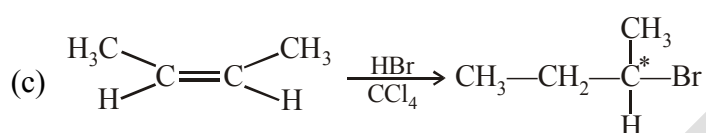
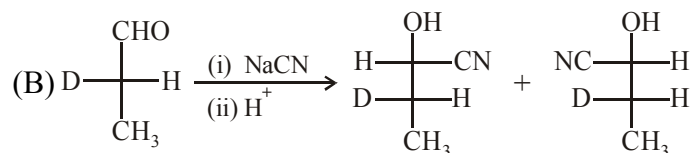
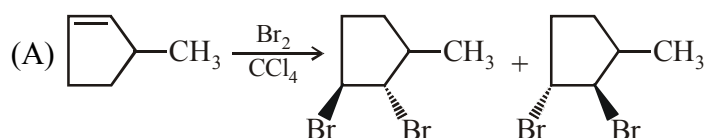
**ANSWER-KEY****EXERCISE # I (MAINS ORIENTED)**

|              |              |              |              |               |
|--------------|--------------|--------------|--------------|---------------|
| 1. Ans. (A)  | 2. Ans. (C)  | 3. Ans. (D)  | 4. Ans. (D)  | 5. Ans. (C)   |
| 6. Ans. (C)  | 7. Ans. (B)  | 8. Ans. (D)  | 9. Ans. (B)  | 10. Ans. (B)  |
| 11. Ans. (C) | 12. Ans. (C) | 13. Ans. (C) | 14. Ans. (A) | 15. Ans. (D)  |
| 16. Ans. (B) | 17. Ans. (A) | 18. Ans. (D) | 19. Ans. (C) | 20. Ans. (D)  |
| 21. Ans. (D) | 22. Ans. (A) | 23. Ans. (D) | 24. Ans. (A) | 25. Ans. (B)  |
| 26. Ans. (C) | 27. Ans. (B) | 28. Ans. (C) | 29. Ans. (D) | 30. Ans. (B)  |
| 31. Ans. (D) | 32. Ans. (B) | 33. Ans. (B) | 34. Ans. (C) | 35. Ans. (A)  |
| 36. Ans. (A) | 37. Ans. (C) | 38. Ans. (D) | 39. Ans. (A) | 40. Ans. (B)  |
| 41. Ans. (B) | 42. Ans. (C) | 43. Ans. (A) | 44. Ans. (C) | 45. Ans. (A)  |
| 46. Ans. (C) | 47. Ans. (D) | 48. Ans. (D) | 49. Ans. (B) | 50. Ans. (C)  |
| 51. Ans. (B) | 52. Ans. (C) | 53. Ans. (A) | 54. Ans. (C) | 55. Ans. (A)  |
| 56. Ans. (D) | 57. Ans. (C) | 58. Ans. (B) | 59. Ans. (B) | 60. Ans. (C)  |
| 61. Ans. (C) | 62. Ans. (D) | 63. Ans. (A) | 64. Ans. (B) | 65. Ans. (A)  |
| 66. Ans. (C) | 67. Ans. (D) | 68. Ans. (B) | 69. Ans. (B) | 70. Ans. (C)  |
| 71. Ans. (B) | 72. Ans. (C) | 73. Ans. (C) | 74. Ans. (A) | 75. Ans. (B)  |
| 76. Ans. (A) | 77. Ans. (A) | 78. Ans. (D) | 79. Ans. (C) | 80. Ans. (B)  |
| 81. Ans. (C) | 82. Ans. (C) | 83. Ans. (C) | 84. Ans. (B) | 85. Ans. (D)  |
| 86. Ans. (C) | 87. Ans. (B) | 88. Ans. (A) | 89. Ans. (C) | 90. Ans. (C)  |
| 91. Ans. (A) | 92. Ans. (C) | 93. Ans. (B) | 94. Ans. (B) | 95. Ans. (A)  |
| 96. Ans. (B) | 97. Ans. (D) | 98. Ans. (B) | 99. Ans. (B) | 100. Ans. (D) |

**EXERCISE # II (A)**

|                   |                  |                  |                  |
|-------------------|------------------|------------------|------------------|
| 1. Ans. (A,B,C,D) | 2. Ans. (A,B,C)  | 3. Ans. (A,B)    | 4. Ans. (B,D)    |
| 5. Ans. (B,D)     | 6. Ans. (A,C)    | 7. Ans. (A,C,D)  | 8. Ans. (A,C)    |
| 9. Ans. (A,B,D)   | 10. Ans. (A,C)   | 11. Ans. (A,B,D) | 12. Ans. (A,C,D) |
| 13. Ans. (A,CD)   | 14. Ans. (A,B,C) | 15. Ans. (A,C,D) | 16. Ans. (B,D)   |
| 17. Ans. (B,D)    | 18. Ans. (A,B)   | 19. Ans. (A,B,C) | 20. Ans. (C,D)   |
| 21. Ans. (B,C)    | 22. Ans. (B,C,D) |                  |                  |

23. Ans.



24. Ans. (A,B)

25. Ans. (A,C)

26. Ans. (A,B,D)

27. Ans. (A,B,C,D)

28. Ans. (A,B,C,D)

29. Ans. (B)

30. Ans. (A,B,C)

31. Ans. (A,C)

## EXERCISE # II (B)

1. Ans. (C)

2. Ans. (C)

3. Ans. (B)

4. Ans. (A) → P, R ; (B) → P, Q ; (C) → P ; (D) → P, Q

5. Ans. (A) → Q ; (B) → P ; (C) → S ; (D) → R

6. Ans. (A) → S ; (B) → Q ; (C) → R ; (D) → P

7. Ans. (A) → S ; (B) → R, S ; (C) → R ; (D) → P, Q

8. Ans. (A) → P, Q, R, S ; (B) → P, R ; (C) → P, T ; (D) → Q, S

9. Ans. (A) → Q, S ; (B) → P, R, S ; (C) → P, R, S ; (D) → P, Q, R, S

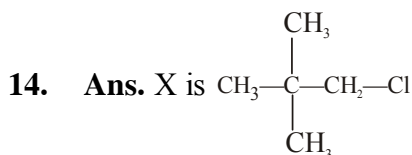
10. Ans. (A) → S, T ; (B) → P, S, T ; (C) → U ; (D) → Q ; (E) → T, U

11. Ans. (A) → R ; (B) → Q, S ; (C) → P, Q ; (D) → Q, S

12. Ans. (A) → P ; (B) → P ; (C) → Q ; (D) → R

13. Ans.

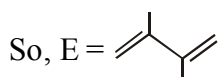
C-I bond being less stable than C-Cl bond and thus on heating heterolytic cleavage of C-I form  $I^-$  which gives yellow precipitate with  $AgNO_3$ .



15. Ans. Molecule A,  $C_6H_{11}Br$  has 1 unsaturation

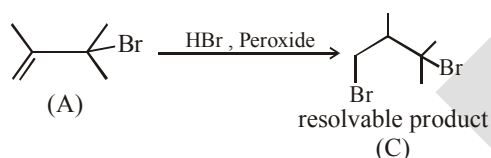


A single possible product, it suggests a symmetrical arrangement



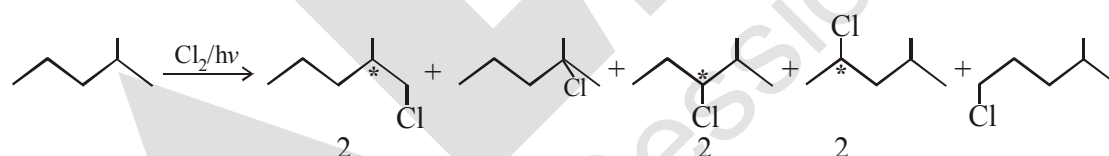
There are only two possibilities of A  $\begin{array}{c} \diagup \\ \diagdown \end{array}CH_2Br$  or  $\begin{array}{c} \diagup \\ \diagdown \end{array}Br$  structure I can be resolved

while structure II cannot be resolved so 'A' :

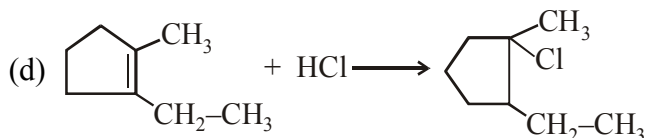
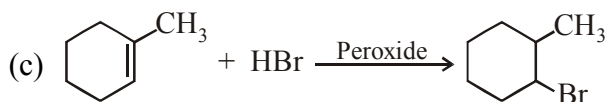
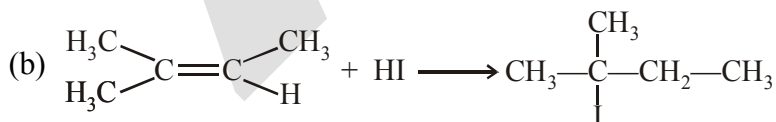


16. Ans. Both step is exothermic with HBr

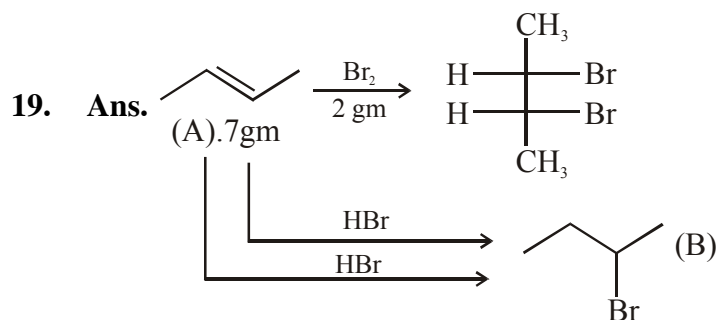
17. Ans.



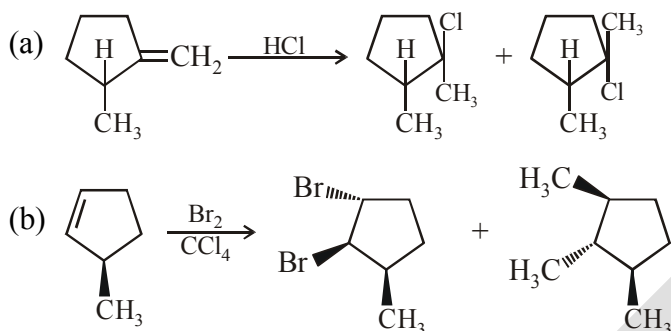
18. Ans.







20. Ans.

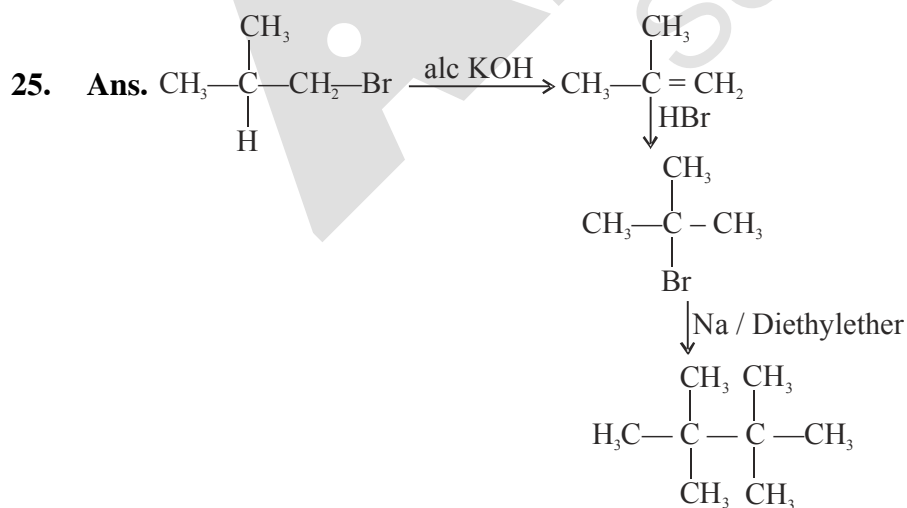
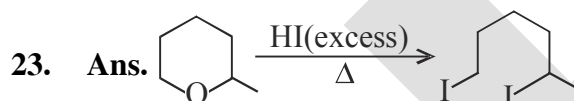


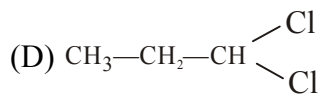
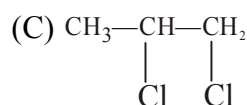
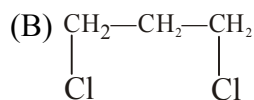
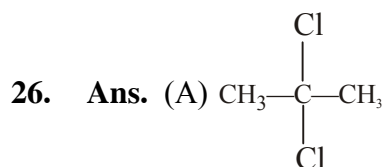
21. Ans.

The elimination of HI (or DI) in presence of strong base shows E2 elimination. The rate determining step involves breaking up of C – H (or C–D) bond. The C–D bond being stronger than C–H and thus elimination is faster in case of  $\text{CH}_3 - \text{CH}_2\text{I}$ .

22. Ans.

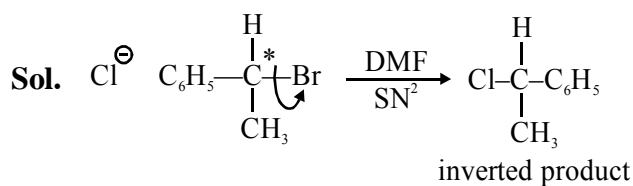
In second compound  $\pi$  bonds are conjugated so due to resonance given product is formed as major product.



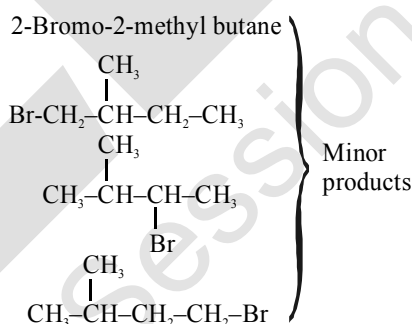
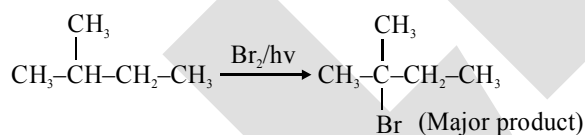


### EXERCISE # III (J-MAINS)

1. Ans. (3)                      2. Ans. (1)                      3. Ans. (1)                      4. Ans. (2)  
5. Ans. (4)                      6. Ans. (2)                      7. Ans. (2)                      8. Ans. (4)  
9. Ans. (4)



- 10. Ans. (1)**  
**Sol.**

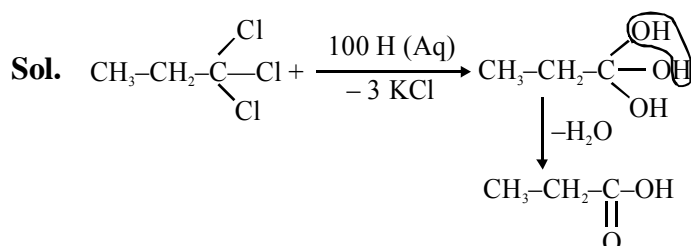


selectivity ratio for bromination is

$$1^\circ : 2^\circ : 3^\circ :: 1 : 82 : 1600$$

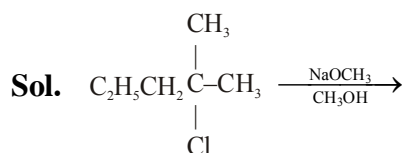
Hence 3° product will be major product.

11. Ans. (2)  
12. Ans. (2)

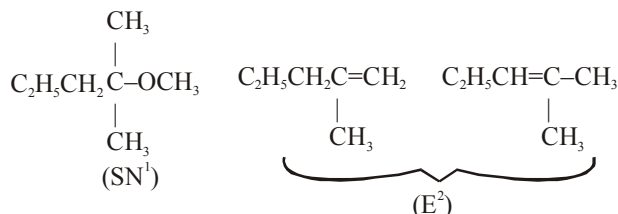


13. Ans. (2)

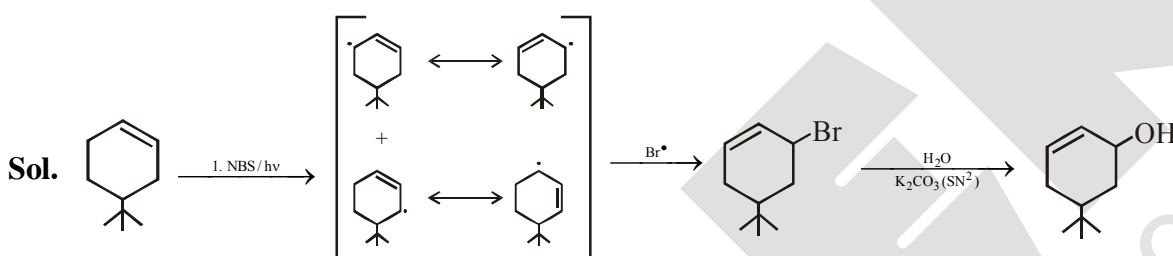
14. Ans. (2)



possible mechanism which takes place is  $\text{E}^2$  &  $\text{SN}^1$  mechanism. Hence possible products are.

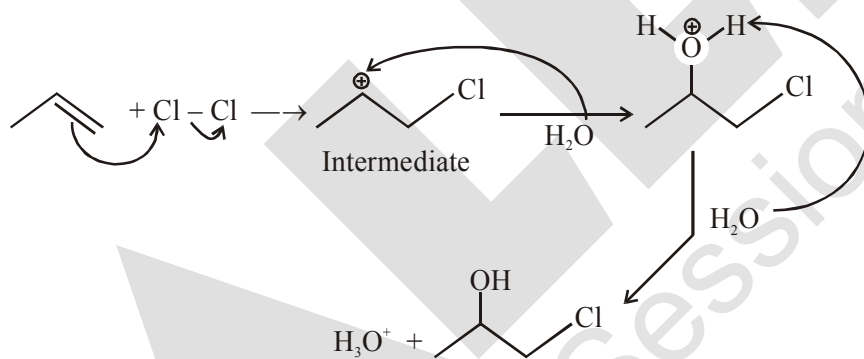


15. Ans. (3)



16. Ans. (3)

Sol.



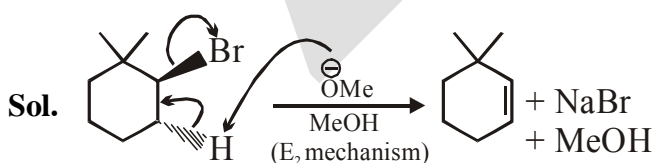
17. Ans. (2)

18. Ans. (1)

19. Ans. (4)

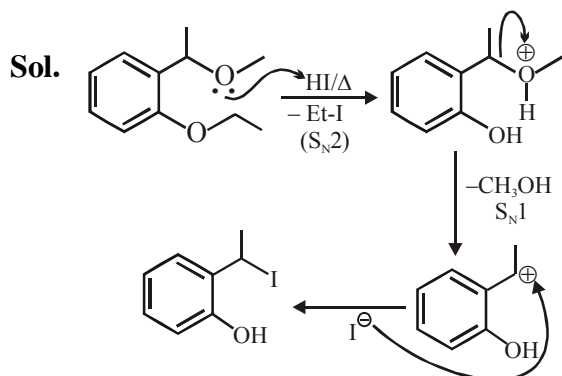
20. Ans. (2)

21. Ans. (1)



Reaction is dehydrohalogenation  $\text{E}^2$ -elimination reaction. Elimination takes place in single step and proceed by formation of transition state from anti position.

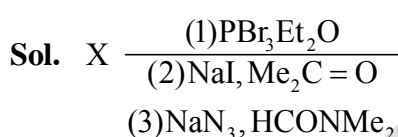
22. Ans. (3)



It is nucleophilic substitution reaction.

### EXERCISE # IV (A) (J-ADVANCE OBJECTIVE)

- |                                                      |               |              |              |              |
|------------------------------------------------------|---------------|--------------|--------------|--------------|
| 1. Ans. (D)                                          | 2. Ans. (B,D) | 3. Ans. (A)  | 4. Ans. (C)  | 5. Ans. (B)  |
| 6. Ans. (A)                                          | 7. Ans. (A,C) | 8. Ans. (D)  | 9. Ans. (C)  | 10. Ans. (D) |
| 11. Ans. (A)                                         | 12. Ans. (B)  | 13. Ans. (D) | 14. Ans. (B) | 15. Ans. (A) |
| 16. Ans. (A) → Q ; (B) → Q ; (C) → R, S ; (D) → P, S |               |              |              |              |
| 17. Ans. (A)                                         | 18. Ans. (D)  | 19. Ans. (B) | 20. Ans. (D) | 21. Ans. (5) |
| 22. Ans. (B)                                         |               |              |              |              |

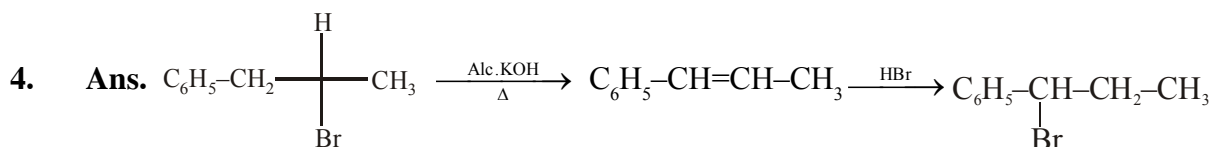
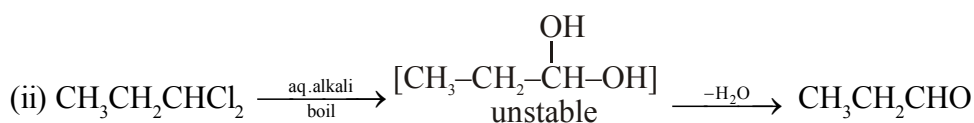
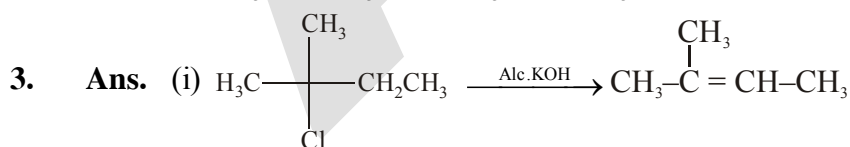


all the three reaction are  $S_N2$  so X is

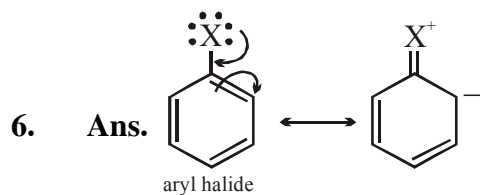


### EXERCISE # IV (B) (J-ADVANCE SUBJECTIVE)

1. Ans. (a) propyl chloride, (b) ortho  
 2. Ans. (i)  $H_2O < CH_3OH < HO^- < CH_3O^-$   
 (ii)  $CH_3F < CH_3Cl < CH_3Br < CH_3I$

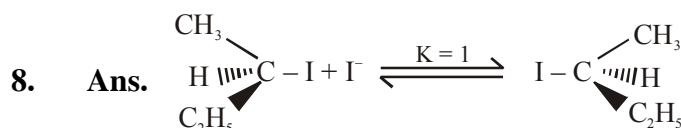
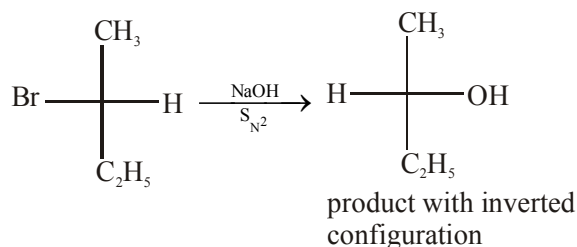


5. Ans. (i)  $\text{C}_6\text{H}_5 - \text{CH} = \text{CH} - \text{CH}_3$  ;  $\text{C}_6\text{H}_5 - \overset{\text{Br}}{\underset{|}{\text{CH}}} - \text{CH}_2 - \text{CH}_3$  (ii)  $\text{C}_6\text{H}_5\text{COOMgI} + \text{CH}_4$



Due to the above resonance phenomena, C-X bond acquire partial double bond character and becomes difficult to break in the rate determining step of  $\text{S}_{\text{N}}2$  reaction.

7. Ans.  $\text{S}_{\text{N}}2$  reactions leads to inversion of configuration at a-C.



Above equilibrium is established which has equilibrium constant equal to 1. Therefore, equilibrium mixture will have both the enantiomers in equal amount giving racemic mixture.

